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To:
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Date of mailing *(day/month/year)* **23 June 2005 (23.06.2005)**	
Applicant's or agent's file reference **62226-PCT-AM2**	**IMPORTANT NOTIFICATION**
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Applicant
BLACKLIGHT POWER, INC. et al

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Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
05 January 2004 (05.01.2004)	60/534,112	US	09 February 2005 (09.02.2005)
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The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. +41 22 338 82 70	Authorized officer **Christelle CROCI (Fax : 338 89 75)** Facsimile No. (41-22) 338.89.75 Telephone No. +41 22 338 9933

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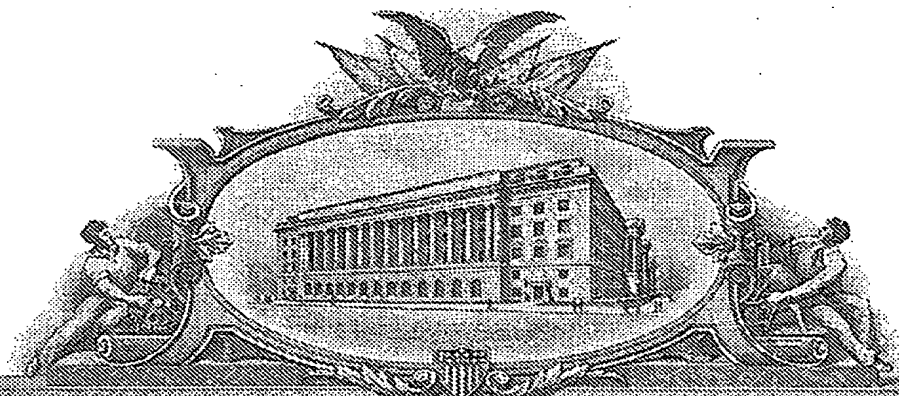
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APPLICATION NUMBER: *60/542,278*
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15535 U.S. PTO
60/542278
020904

Sir:

Herewith is a <u>PROVISIONAL APPLICATION</u>

Title: ATOM MODELS AND APPLICATIONS

Our Order No. _____ **62226**
50-0687

| C# | M# |

Atty. Dkt. _____ **62226-P-AM2**

| M# | Client Ref |

including:

Date: 9 February 2004

1. Specification: __**132**__ pages   2. ☐ Specification in non-English   3. ☐ Drawings: _____ sheet(s)

4. The invention ☐ was ☒ was not made by, or under a contract with, an agency of the U.S. Government.
   If yes, Government agency/contact # = _____

5. ☐ Attached is an assignment and cover sheet. <u>Please return the recorded assignment</u> to the undersigned.

6. ☒ Applicant(s) claims "small entity" status under Rules 9 & 27.

7. ☐ Attached:

8. This application is made by the following named inventor(s) (Double check instructions for accuracy.):

(1) Inventor	Randell	L.	Mills
	First	Middle Initial	Family Name
Residence	Cranbury		New Jersey
	City		State/Foreign Country

(2) Inventor			
	First	Middle Initial	Family Name
Residence			
	City		State/Foreign Country

(3) Inventor			
	First	Middle Initial	Family Name
Residence			
	City		State/Foreign Country

(4) Inventor			
	First	Middle Initial	Family Name
Residence			
	City		State/Foreign Country

(5) Inventor			
	First	Middle Initial	Family Name
Residence			
	City		State/Foreign Country

	Large/Small Entity		Fee Code
10. Filing Fee	$80	$80	114/214
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Manelli Denison & Selter, PLLC By: Atty: **Jeffrey S. Melcher**   Reg. No.   **35,950**

Customer No.: 20736

Sig: Fax: (202) 887-0336

Tel: (202)261-1045

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APPLICATION UNDER UNITED STATES PATENT LAWS

Invention: **ATOM MODELS AND APPLICATIONS**

Inventor(s): Randell L. Mills

Attorney Docket No: 62226-AM2

Jeffrey S. Melcher
Manelli, Denison & Selter P.L.L.C.
Customer No.: 20736
2000 M Street, N.W.
7th Floor
Washington, D.C. 20036-3307

THIS IS A PROVISIONAL PATENT APPLICATION

SPECIFICATION

THREE, FOUR, FIVE, SIX, SEVEN, EIGHT, NINE, TEN, ELEVEN, TWELVE, THIRTEEN, FOURTEEN, FIFTEEN, SIXTEEN, SEVENTEEN, EIGHTEEN, NINETEEN, AND TWENTY-ELECTRON ATOMS

THREE-ELECTRON ATOMS

As is the case for one and two-electron atoms shown in the corresponding sections, three through ten-electron atoms can also be solved exactly using the results of the solutions of the preceding atoms. For example, three-electron atoms can be solved exactly using the results of the solutions of the one and two-electron atoms.

THE LITHIUM ATOM

For Li^+, there are two spin-paired electrons in an orbitsphere with

$$r_1 = r_2 = a_o \left[\frac{1}{2} - \frac{\sqrt{\frac{3}{4}}}{6} \right] \quad (10.1)$$

as given by Eq. (7.19) where r_n is the radius of electron n which has velocity v_n. The next electron is added to a new orbitsphere because of the repulsive diamagnetic force between the two spin-paired electrons and the spin-unpaired electron. This repulsive diamagnetic force is due to the interaction of the magnetic field of the outer spin-unpaired electron on the electron current of the two spin-paired electrons of the inner shell. The diamagnetic force on the outer electron is determined by first considering the central force on each electron of the inner shell due to the magnetic flux B of the outer electron that follows from Purcell [1]

$$\mathbf{F} = \frac{2m_e v_n \Delta v}{r} \mathbf{i}_r \quad (10.2)$$

where $\mathbf{i}_r$ is defined as the radial vector in the direction of the central electric field of the nucleus and

$$\frac{\Delta v}{r} = \frac{eB}{2m_e} \quad (10.3)$$

The velocity v_n is given by the boundary condition for no radiation as follows:

$$v_1 = \frac{\hbar}{m_e r_1} \quad (10.4)$$

where r_1 is the radius of the first orbitsphere; therefore, the force on each of the inner electrons is given as follows:

$$\mathbf{F} = \frac{\hbar eB}{m_e r_1} \mathbf{i}_r \quad (10.5)$$

The change in magnetic moment, Δm, of each electron of the inner shell

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due to the magnetic flux B of the outer electron is [1]

$$\Delta m = -\frac{e^2 r_1^2 B}{4 m_e} \qquad (10.6)$$

The diamagnetic force on the outer electron due to the two inner shell electrons is in the opposite direction of the force given by Eq. (10.5), and this diamagnetic force on the outer electron is proportional to the sum of the changes in magnetic moments of the two inner electrons due to the magnetic flux B of the outer electron. The two electrons are spin-paired and the, .   Thus, the change in velocity of each electron treated individually (Eq. (10.3)) due to the magnetic flux B would be equal and opposite.   However, the two paired electrons may be treated as one with twice the mass where m_e is replaced by $2m_e$ in Eq. (10.6).   In this case, the paired electrons spin together about the field axis to cause a reduction in the flux according to Lenz's law.   It is then apparent that the force given by Eq. (10.5) is proportional to the flux B of the outer electron; whereas, the total of the change in magnetic moments of the inner shell electrons given by Eq. (10.6) applied to the combination of the inner electrons is proportional to one eighth of the flux, B.   Thus, the force on the outer electron due to the reaction of the inner shell to the flux of the outer electron is given as follows:

$$\mathbf{F}_{diamagnetic} = -\frac{\hbar}{8 r_1} \frac{eB}{m_e} \mathbf{i}_r \qquad (10.7)$$

where r_1 is the radial distance of the first orbitsphere from the nucleus. The magnetic flux, B, is supplied by the constant field inside the orbitsphere of the outer electron at radius r_3 and is given by the product of μ_o times Eq. (1.120).

$$B = \frac{\mu_o e \hbar}{m_e r_3^3} \qquad (10.8)$$

The result of substitution of Eq. (10.8) into Eq. (10.7) is

$$\mathbf{F}_{diamagnetic} = -\left[\frac{e^2 \mu_o}{2 m_e r_3}\right] \frac{\hbar^2}{4 m_e r_1 r_3^2} \mathbf{i}_r \qquad (10.9)$$

The term in brackets can be expressed in terms of the fine structure constant, α.   From Eqs. (1.144-1.148)

$$\frac{e^2 \mu_o}{2 m_e r_3} = 2\pi\alpha \frac{v}{c} \qquad (10.10)$$

It is demonstrated in the Two Electron Atom section that the relativistic correction to Eq. (10.9) is $\frac{1}{Z}$ times the reciprocal of Eq. (10.10). Z for electron three is one; thus, one is substituted for the term in brackets in Eq. (10.9).

The force must be corrected for the vector projection of the velocity

onto the z-axis.   As given in the Spin Angular Momentum of the Orbitsphere with $\ell = 0$ section, the application of a z directed magnetic field of electron three given by Eq. (1.120) to the two inner orbitspheres gives rise to a diamagnetic field and a projection of the angular momentum of electron three onto an axis which precesses about the z-axis of $\sqrt{\frac{3}{4}}\hbar$.   The projection of the force between electron three and electron one and two is equivalent to that of the angular momentum onto the axis which precesses about the z-axis, and is $\sqrt{s(s+1)} = \sqrt{\frac{3}{4}}$ times that of a point mass.   Thus, Eq. (10.9) becomes

$$\mathbf{F}_{diamagnetic} = -\frac{\hbar^2}{4m_e r_3^2 r_1} \sqrt{s(s+1)}\mathbf{i}_r \qquad (10.11)$$

THE RADIUS OF THE OUTER ELECTRON OF THE LITHIUM ATOM

The radius for the outer electron is calculated by equating the outward centrifugal force to the sum of the electric and diamagnetic forces as follows:

$$\frac{m_e v_3^2}{r_3} = \frac{e^2}{4\pi\varepsilon_o r_3^2} - \frac{\hbar^2}{4m_e r_3^2 r_1}\sqrt{s(s+1)} \qquad (10.12)$$

With $v_3 = \frac{\hbar}{m_e r_3}$ (Eq. (1.56), $r_1 = a_o\left[\frac{1}{2} - \frac{\sqrt{\frac{3}{4}}}{6}\right]$ (Eq. (7.19)), and $s = \frac{1}{2}$, we solve for

r_3.

$$r_3 = \frac{a_o}{\left[1 - \dfrac{\sqrt{3/4}}{4\left(\dfrac{1}{2} - \dfrac{\sqrt{3/4}}{6}\right)}\right]} \qquad (10.13)$$

$$r_3 = 2.5559\, a_o$$

THE IONIZATION ENERGY OF LITHIUM

From Eq. (1.233), the magnitude of the energy stored in the electric field is

$$\frac{e^2}{8\pi\varepsilon_o r_3} = 5.318\, eV \qquad (10.14)$$

The magnetic field of the outer electron changes the angular velocities of the inner electrons.   However, the magnetic field of the outer electron

provides a central Lorentzian force which exactly balances the change in centrifugal force because of the change in angular velocity [1]. Thus, the electric energy of the inner orbitsphere is unchanged upon ionization. The magnetic field of the outer electron, however, also changes the magnetic moment, m, of each of the inner orbitsphere electrons. From Eq. (10.6), the change in magnetic moment, Δm, (per electron) is

$$\Delta m = -\frac{e^2 r_1^2}{4m_e} B \qquad (10.15)$$

where B is the magnetic flux of the outer electron given by the product of μ_o times Eq. (1.120).

$$B = \frac{\mu_o e \hbar}{m_e r_3^3} \qquad (10.16)$$

Substitution of Eq. (10.16) and $2m_e$ for m_e (because there are two electrons) into Eq. (10.15) gives

$$\Delta m = -\left[\frac{e^2 \mu_o}{2m_e r_3}\right]\frac{e\hbar r_1^2}{4m_e r_3^2} \qquad (10.17)$$

Furthermore, we know from Eqs. (10.9) and (10.11) that the term in brackets is replaced by $\sqrt{s(s+1)}$.

$$\Delta m = -\frac{e\hbar r_1^2}{4m_e r_3^2}\sqrt{s(s+1)} \qquad (10.18)$$

Substitution of Eq. (10.1) for r_1, Eq. (10.13) for r_3, and given that the magnetic moment of an electron is one Bohr magneton according to Eq. (1.99),

$$\mu_B = \frac{e\hbar}{2m_e} \qquad (10.19)$$

the fractional change in magnetic moment of an inner shell electron, Δm_f, is given as follows:

$$\Delta m_f = \frac{\dfrac{e\hbar r_1^2 \sqrt{s(s+1)}}{4m_e r_3^2}}{\dfrac{e\hbar}{2m_e}} \qquad (10.20)$$

$$= \frac{1}{2}\frac{r_1^2}{r_3^2}\sqrt{s(s+1)} \qquad (10.21)$$

With r_1 given by Eq. (10.1), r_3 given by Eq. (10.13), and $s = \frac{1}{2}$, the fractional change in magnetic moment of the two inner shell electrons is

$$\Delta m_f = \frac{\left[\left[a_o\left[\frac{1}{2}-\frac{\sqrt{\frac{3}{4}}}{6}\right]\right]^2\sqrt{\frac{3}{4}}\right]}{\left[1-\cfrac{a_o}{\cfrac{\sqrt{\frac{3}{4}}}{4\left(\frac{1}{2}-\frac{\sqrt{\frac{3}{4}}}{6}\right)}}\right]^2}$$

(10.22)

$$\Delta m_f = 0.01677$$

We add one (corresponding to m_f) to Δm_f which is the fractional change in the magnetic moment.   The energy stored in the magnetic field is proportional to the magnetic field strength squared as given by Eq. (1.122); thus, the sum is squared

$$(1.0168)^2 = 1.03382$$

(10.23)

Thus, the change in magnetic energy of the inner orbitsphere is 3.382 %, so that the corresponding energy ΔE_{mag} is

$$\Delta E_{mag} = 0.03382 \, X \, 2.543 \, eV = 0.0860 \, eV$$

(10.24)

where the magnetic energy of the inner electrons given in Table 7.1 is 2.543 eV.   Then the ionization energy of the lithium atom is given by Eqs. (10.13-10.14) and (10.24):

$$E(ionization; \, Li) = \frac{(Z-2)e^2}{8\pi\varepsilon_o r_3} + \Delta E_{mag}$$

(10.25)

$$= 5.3178 \, eV + 0.0860 \, eV = 5.4038 \, eV$$

The experimental ionization energy of lithium is 5.392 eV [2-3].

THREE-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>3

Three-electron atoms having $Z > 3$ possess an electric field of

$$\mathbf{E} = \frac{(Z-3)e}{4\pi\varepsilon_o r^2}\mathbf{i}_r$$

(10.26)

for $r > r_3$. For three-electron atoms having $Z > 3$, the diamagnetic force given by Eq. (10.11) is unchanged.   However, for three-electron atoms having $Z > 3$, an electric field exists for $r > r_3$. This electric field gives rise

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to an additional diamagnetic force term which adds to Eq. (10.11).   The
additional diamagnetic force is derived as follows.   The diamagnetic force
repels the third (outer) electron, and the electric force attracts the third
electron.   Consider the reverse of ionization where the third electron is at
infinity and the two spin paired electrons are at $r_1 = r_2$ given by Eq. (7.19).

Power must be conserved as the net force of the diamagnetic and
electric forces cause the third electron to move from infinity to its final
radius.   Power flow is given by the Poynting Power Theorem:

$$\nabla \bullet (\mathbf{E} \times \mathbf{H}) = -\frac{\delta}{\delta t}\left[\frac{1}{2}\mu_o \mathbf{H} \bullet \mathbf{H}\right] - \frac{\delta}{\delta t}\left[\frac{1}{2}\varepsilon_o \mathbf{E} \bullet \mathbf{E}\right] - \mathbf{J} \bullet \mathbf{E} \tag{10.27}$$

During binding, the radius of electron three decreases.   The electric force

$$\mathbf{F}_{ele} = \frac{(Z-2)e^2}{4\pi\varepsilon_o r_3^2}\mathbf{i}_r \tag{10.28}$$

increases the stored electric energy which corresponds to the power
term, $-\frac{\delta}{\delta t}\left[\frac{1}{2}\varepsilon_o \mathbf{E} \bullet \mathbf{E}\right]$, of Eq. (10.27).   The diamagnetic force given by Eq.
(10.7) changes the stored magnetic energy which corresponds to the
power term, $-\frac{\delta}{\delta t}\left[\frac{1}{2}\mu_o \mathbf{H} \bullet \mathbf{H}\right]$, of Eq. (10.27).   An additional diamagnetic
force arises when $Z - 3 > 0$.   This diamagnetic force corresponds to that
given by Purcell [1] for a charge moving in a central field having an
imposed magnetic field perpendicular to the plane of motion.   The second
diamagnetic force $\mathbf{F}_{diamagnetic\ 2}$ is given by

$$\mathbf{F}_{diamagnetic\ 2} = -2\frac{m_e \Delta v^2}{r_1}\mathbf{i}_r \tag{10.29}$$

where Δv is derived from Eq. (10.3).   The result of substitution of Δv into
Eq. (10.29) is

$$\mathbf{F}_{diamagnetic\ 2} = -\frac{2m_e}{r_1}\left[\frac{er_1 B}{2m_e}\right]^2 \mathbf{i}_r \tag{10.30}$$

The magnetic flux, B, at electron three for $r < r_3$ is given by the product of
μ_o times Eq. (1.120).   The result of the substitution of the flux into Eq.
(10.30) is

$$\mathbf{F}_{diamagnetic\ 2} = -2\left[\frac{e^2\mu_o}{2m_e r_3}\right]^2 \frac{r_1 \hbar^2}{m_e r_3^4}\mathbf{i}_r \tag{10.31}$$

The term in brackets can be expressed in terms of the fine structure
constant, α.   From Eqs. (1.144-1.148)

$$\frac{Z_1 e^2 \mu_o}{2m_e r_3} = 2\pi\alpha Z_1 \frac{v}{c} \tag{10.32}$$

It is demonstrated in the Two Electron Atom section that the relativistic

correction to Eq. (10.31) is $\dfrac{1}{Z}$ times the reciprocal of Eq. (10.32).   Consider the case wherein Z_1 of Eq. (10.32) is different from $Z = Z_2$ of Eq. (7.13) in order to maintain relativistic invariance of the electron angular momentum and magnetic moment.   The relativistic correction to Eq. (10.31) can be considered the product of two corrections—a correction of electron three relative to electron one and two and electron one and two relative to electron three.   In the former case, Z_1 and $Z_2 = 1$ which corresponds to electron three.   In the latter case, $Z_1 = Z - 3$, and $Z_2 = Z - 2$ which corresponds to r_3^+, infinitesimally greater than the radius of the outer orbitsphere and r_3^-, infinitesimally less than the radius of the outer orbitsphere, respectively, where Z is the nuclear charge.   Thus, $\dfrac{Z-3}{Z-2}$ is substituted for the term in brackets in Eq. (10.31).   The force must be corrected for the vector projection of the velocity onto the z-axis.   As given in the Spin Angular Momentum of the Orbitsphere with $\ell = 0$ section, the application of a z directed magnetic field of electron three given by Eq. (1.120) to the two inner orbitspheres gives rise to a diamagnetic field and a projection of the angular momentum of electron three onto an axis which precesses about the z-axis of $\sqrt{\dfrac{3}{4}}\hbar$.   The projection of the force between electron three and electron one and two is equivalent to that of the angular momentum onto the axis which precesses about the z-axis, and is $\sqrt{s(s+1)} = \sqrt{\dfrac{3}{4}}$ times that of a point mass. Thus, Eq. (10.31) becomes

$$\mathbf{F}_{diamagnetic\ 2} = -2\frac{(Z-3)r_1\hbar^2}{(Z-2)m_e r_3^4}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.33)$$

As given previously in the Two Electron section, this force corresponds to the dissipation term of Eq. (10.27), $\mathbf{J} \bullet \mathbf{E}$.   The current $\mathbf{J}$ is proportional to the sum of one for the outer electron and two times two—the number of spin paired electrons.   For the inner electrons, the factor of two arises because they possess mutual inductance which doubles their contribution to $\mathbf{J}$.   (Recall the general relationship that the current is equal to the flux divided by the inductance.)   Thus, the second diamagnetic force is

$$\mathbf{F}_{diamagnetic\ 2} = -2\left[\frac{Z-3}{Z-2}\right]\frac{(1+4)r_1\hbar^2}{m_e r_3^4}\sqrt{s(s+1)}\mathbf{i}_r;\quad s = \frac{1}{2} \qquad (10.34)$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-3}{Z-2}\right]\frac{r_1\hbar^2}{m_e r_3^4}10\sqrt{3/4}\mathbf{i}_r \qquad (10.35)$$

THE RADIUS OF THE OUTER ELECTRON OF THREE-ELECTRON

ATOMS WITH A NUCLEAR CHARGE Z>3

The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric and diamagnetic forces as follows:

$$\frac{m_e v_3^2}{r_3} = \frac{(Z-2)e^2}{4\pi\varepsilon_o r_3^2} - \frac{\hbar^2}{4m_e r_3^2 r_1}\sqrt{s(s+1)} - \left[\frac{Z-3}{Z-2}\right]\frac{r_1 \hbar^2}{r_3^4 m_e}10\sqrt{s(s+1)}$$

(10.36)

With $v_3 = \dfrac{\hbar}{m_e r_3}$ (Eq. (1.56), $r_1 = a_0\left(\dfrac{1}{Z-1} - \dfrac{\sqrt{s(s+1)}}{Z(Z-1)}\right)$ (Eq. (7.19), and $s = \dfrac{1}{2}$, we solve for r_3 using the quadratic formula or reiteratively.

$$r_3 = \frac{\left[1+\left[\dfrac{Z-3}{Z-2}\right]\dfrac{r_1}{r_3}10\sqrt{\dfrac{3}{4}}\right]}{\left[\dfrac{(Z-2)}{a_o} - \dfrac{\sqrt{\dfrac{3}{4}}}{4r_1}\right]}$$

(10.37)

The quadratic equation corresponding to Eq. (10.37) is

$$r_3^2 - \frac{r_3}{\left[\dfrac{(Z-2)}{a_o} - \dfrac{\sqrt{\dfrac{3}{4}}}{4r_1}\right]} - \frac{\left[\dfrac{Z-3}{Z-2}\right]r_1 10\sqrt{\dfrac{3}{4}}}{\left[\dfrac{(Z-2)}{a_o} - \dfrac{\sqrt{\dfrac{3}{4}}}{4r_1}\right]} = 0$$

(10.38)

The solution of Eq. (10.38) using the quadratic formula is

$$r_3 = \frac{\left[\dfrac{a_o}{\left[(Z-2)-\dfrac{\sqrt{\dfrac{3}{4}}}{4r_1}\right]}\right] \pm a_o \sqrt{\dfrac{1}{\left[(Z-2)-\dfrac{\sqrt{\dfrac{3}{4}}}{4r_1}\right]^2} + 4\dfrac{\left[\dfrac{Z-3}{Z-2}\right]r_1 10\sqrt{\dfrac{3}{4}}}{\left[(Z-2)-\dfrac{\sqrt{\dfrac{3}{4}}}{4r_1}\right]}}}{2}, \ r_1 \text{ in units of } a_o$$

(10.39)

$$r_3 = \frac{\left[\dfrac{a_o}{\left[(Z-2)-\dfrac{\sqrt{\dfrac{3}{4}}}{4r_1}\right]}\right]\left[1 \pm \sqrt{1 + 4\left[\dfrac{Z-3}{Z-2}\right]r_1 10\sqrt{\dfrac{3}{4}}\left[(Z-2)-\dfrac{\sqrt{\dfrac{3}{4}}}{4r_1}\right]}\right]}{2}, \ r_1 \text{ in units of } a_o$$

(10.40)

$$r_3 = \cfrac{\cfrac{a_o}{\left[(Z-2)-\cfrac{\sqrt{\frac{3}{4}}}{4r_1}\right]}\left[1\pm\sqrt{1+4(Z-3)r_1 10\sqrt{\frac{3}{4}}-\left[\frac{Z-3}{Z-2}\right]\frac{30}{4}}\right]}{2} \quad , r_1 \text{ in units of } a_o \qquad (10.41)$$

$$r_3 = \cfrac{\cfrac{a_o}{\left[(Z-2)-\cfrac{\sqrt{\frac{3}{4}}}{4\left(\frac{1}{Z-1}-\frac{\sqrt{3/4}}{Z(Z-1)}\right)}\right]}\left[1\pm\sqrt{1+4(Z-3)\left(\frac{1}{Z-1}-\frac{\sqrt{3/4}}{Z(Z-1)}\right)10\sqrt{\frac{3}{4}}-\left[\frac{Z-3}{Z-2}\right]\frac{30}{4}}\right]}{2}$$

$$(10.42)$$

The positive root of Eq. (10.42) must be taken in order that $r_3 > 0$.

THE IONIZATION ENERGIES OF THREE-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>3

The energy stored in the electric field, $E(electric)$, is

$$E(electric) = -\frac{(Z-2)e^2}{8\pi\varepsilon_o r_3} \cdot \qquad (10.43)$$

where r_3 is given by Eq. (10.42). The magnetic field of the outer electron changes the velocities of the inner electrons. However, the magnetic field of the outer electron provides a central Lorentzian field which balances the change in centrifugal force because of the change in velocity. Thus, the electric energy of the inner orbitsphere is unchanged upon ionization. The change in the velocities of the inner electrons upon ionization gives rise to a change in kinetic energies of the inner electrons. The change in velocity, Δv, is given by Eq. (10.3)

$$\Delta v = \frac{e r_1 B}{2m_e} \qquad (10.44)$$

Substitution of the flux, B, given by the product of μ_o and Eq. (1.120), into Eq. (10.43) is

$$\Delta v = \left[\frac{e^2 \mu_o}{2 m_e r_1}\right]\frac{r_1^2 \hbar}{m_e r_3^3} \qquad (10.45)$$

It is demonstrated in the One Electron Atom section and the Two Electron Atom section (at Eq. (7.14)) that the relativistic correction to Eq. (10.45) is $\frac{1}{Z}$ times the reciprocal of the term in brackets. In this case, Z corresponding to electron three is one; thus, one is substituted for the

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term in brackets in Eq. (10.45).   Thus, Eq. (10.45) becomes,

$$\Delta v = \frac{r_1^2 \hbar}{r_3^3 m_e} \tag{10.46}$$

where is r_1 given by Eq. (7.19), and r_3 is given by Eq. (10.42). The change in kinetic energy, ΔE_T, of the two inner shell electrons is given by

$$\Delta E_T = 2\frac{1}{2} m_e \Delta v^2 \tag{10.47}$$

The ionization energy is the sum of the electric energy, Eq. (10.43), and the change in the kinetic energy, Eq. (10.47), of the inner electrons.

$$E(Ionization) = E(Electric) + E_T \tag{10.48}$$

The relativistic correction to Eq. (10.48) is given by 1.) relativistically correcting the radius of the inner paired electrons r_1, 2.) using the relativistically corrected r_1 to determine r_3 which is then relativistically corrected.   The relativistically corrected r_1 is given by dividing the radius given Eq. (7.19) by γ^* of Eq. (1.250)

$$r_2 = r_1 = \frac{r_1}{\gamma^*} = \frac{a_0 \left(\dfrac{1}{Z-1} - \dfrac{\sqrt{s(s+1)}}{Z(Z-1)} \right)}{2\pi \sqrt{1 - \left(\dfrac{v}{c}\right)^2} \sin\left[\dfrac{\pi}{2}\left(1 - \left(\dfrac{v}{c}\right)^2\right)^{3/2} \right] + \cos\left[\dfrac{\pi}{2}\left(1 - \left(\dfrac{v}{c}\right)^2\right)^{3/2} \right]}, \quad s = \frac{1}{2} \tag{10.49}$$

where the velocity is given by Eq. (1.56) with the radius given by Eq. (7.19).   Similarly, the relativistically corrected r_3 is given by dividing the radius given Eq. (10.41) by γ^* of Eq. (1.250)

$$r_3 = \frac{r_3}{\gamma^*} = \frac{\dfrac{a_o}{\left[(Z-2) - \dfrac{\sqrt{\frac{3}{4}}}{4r_1} \right]} \left[1 + \sqrt{1 + 4(Z-3)r_1 10\sqrt{\dfrac{3}{4}} - \left[\dfrac{Z-3}{Z-2}\right]\dfrac{30}{4}} \right]}{2\pi \sqrt{1 - \left(\dfrac{v}{c}\right)^2} \sin\left[\dfrac{\pi}{2}\left(1 - \left(\dfrac{v}{c}\right)^2\right)^{3/2} \right] + \cos\left[\dfrac{\pi}{2}\left(1 - \left(\dfrac{v}{c}\right)^2\right)^{3/2} \right]}, \quad r_1 \text{ in units of } a_o \tag{10.50}$$

where r_1 is given by Eq. (10.49) and the velocity is given by (1.56) with the radius given by Eq. (10.42).   The ionization energies are given by Eq. (10.48) wherein the relativistically corrected radii given by Eqs. (10.49-10.50) are used in the sum of the electric energy, Eq. (10.43), and the change in the kinetic energy, Eq. (10.47), of the inner electrons.   The ionization energies for several three-electron atoms are given in Table 10.1.

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Table 10.1. Ionization energies for some three-electron atoms.

3e Atom	Z	r_1 (a_o)[a]	r_3 (a_o)[b]	Electric Energy[c] (eV)	Δv[d] (m/s)	ΔE_T[e] (eV)	Theoretical Ionization Energies[f] (eV)	Experimental Ionization Energies[g] (eV)	Relative Error[h]
Li	3	0.35566	2.55606	5.3230	1.6571E+04	1.5613E-03	5.40381	5.39172	-0.00224
Be^+	4	0.26116	1.49849	18.1594	4.4346E+04	1.1181E-02	18.1706	18.21116	0.00223
B^{2+}	5	0.20670	1.07873	37.8383	7.4460E+04	3.1523E-02	37.8701	37.93064	0.00160
C^{3+}	6	0.17113	0.84603	64.3278	1.0580E+05	6.3646E-02	64.3921	64.4939	0.00158
N^{4+}	7	0.14605	0.69697	97.6067	1.3782E+05	1.0800E-01	97.7160	97.8902	0.00178
O^{5+}	8	0.12739	0.59299	137.6655	1.7026E+05	1.6483E-01	137.8330	138.1197	0.00208
F^{6+}	9	0.11297	0.51621	184.5001	2.0298E+05	2.3425E-01	184.7390	185.186	0.00241
Ne^{7+}	10	0.10149	0.45713	238.1085	2.3589E+05	3.1636E-01	238.4325	239.0989	0.00279
Na^{8+}	11	0.09213	0.41024	298.4906	2.6894E+05	4.1123E-01	298.9137	299.864	0.00317
Mg^{9+}	12	0.08435	0.37210	365.6469	3.0210E+05	5.1890E-01	366.1836	367.5	0.00358
Al^{10+}	13	0.07778	0.34047	439.5790	3.3535E+05	6.3942E-01	440.2439	442	0.00397
Si^{11+}	14	0.07216	0.31381	520.2888	3.6868E+05	7.7284E-01	521.0973	523.42	0.00444
P^{12+}	15	0.06730	0.29102	607.7792	4.0208E+05	9.1919E-01	608.7469	611.74	0.00489
S^{13+}	16	0.06306	0.27132	702.0535	4.3554E+05	1.0785E+00	703.1966	707.01	0.00539
Cl^{14+}	17	0.05932	0.25412	803.1158	4.6905E+05	1.2509E+00	804.4511	809.4	0.00611
Ar^{15+}	18	0.05599	0.23897	910.9708	5.0262E+05	1.4364E+00	912.5157	918.03	0.00601
K^{16+}	19	0.05302	0.22552	1025.6241	5.3625E+05	1.6350E+00	1027.3967	1033.4	0.00581
Ca^{17+}	20	0.05035	0.21350	1147.0819	5.6993E+05	1.8468E+00	1149.1010	1157.8	0.00751
Sc^{18+}	21	0.04794	0.20270	1275.3516	6.0367E+05	2.0720E+00	1277.6367	1287.97	0.00802
Ti^{19+}	22	0.04574	0.19293	1410.4414	6.3748E+05	2.3106E+00	1413.0129	1425.4	0.00869
V^{20+}	23	0.04374	0.18406	1552.3606	6.7135E+05	2.5626E+00	1555.2398	1569.6	0.00915
Cr^{21+}	24	0.04191	0.17596	1701.1197	7.0530E+05	2.8283E+00	1704.3288	1721.4	0.00992
Mn^{22+}	25	0.04022	0.16854	1856.7301	7.3932E+05	3.1077E+00	1860.2926	1879.9	0.01043
Fe^{23+}	26	0.03867	0.16172	2019.2050	7.7342E+05	3.4011E+00	2023.1451	2023	-0.00007
Co^{24+}	27	0.03723	0.15542	2188.5585	8.0762E+05	3.7084E+00	2192.9020	2219	0.01176
Ni^{25+}	28	0.03589	0.14959	2364.8065	8.4191E+05	4.0300E+00	2369.5803	2399.2	0.01235
Cu^{26+}	29	0.03465	0.14418	2547.9664	8.7630E+05	4.3661E+00	2553.1987	2587.5	0.01326

[a] Radius of the paired inner electrons of three-electron atoms from Eq. (10.49).

[b] Radius of the unpaired outer electron of three-electron atoms from Eq. (10.50).

[c] Electric energy of the outer electron of three-electron atoms from Eq. (10.43).

[d] Change in the velocity of the paired inner electrons due to the unpaired outer electron of three-electron atoms from Eq. (10.46).

[e] Change in the kinetic energy of the paired inner electrons due to the unpaired outer electron of three-electron atoms from Eq. (10.47).

[f] Calculated ionization energies of three-electron atoms from Eq. (10.48) for $Z > 3$ and Eq. (10.25) for Li.

[g] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

[h] (Experimental-theoretical)/experimental.

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The agreement between the experimental and calculated values of Table 10.1 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy.   In this case, the experimental capability is three to four significant figures which is consistent with the last column.   The lithium atom isoelectronic series is given in Table 10.1 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of Li isoelectronic and Rydberg series, as well as direct experimental data.

FOUR-ELECTRON ATOMS

Four-electron atoms can be solved exactly using the results of the solutions of one, two, and three-electron atoms.

RADII OF THE OUTER ELECTRONS OF FOUR-ELECTRON ATOMS

For each three-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19):

$$r_1 = r_2 = a_o \left[\frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)} \right] \tag{10.51}$$

and an unpaired electron with a radius r_3 given by Eq. (10.42).   For $Z \geq 4$, the next electron which binds to form the corresponding four-electron atom becomes spin-paired with the outer electron such that they become indistinguishable with the same radius $r_3 = r_4$.   The corresponding spin-pairing force $\mathbf{F}_{mag}$ is given by Eq. (7.15):

$$\mathbf{F}_{mag} = \frac{1}{Z} \frac{\hbar^2}{m_e r_4^3} \sqrt{s(s+1)} \mathbf{i}_r \tag{10.52}$$

The central forces given by Eq. (10.36) and Eq. (10.52) act on the outer electron to cause it to bind wherein the electric force on the outer-most electron due to the nucleus and the inner three electrons is given by Eq. (10.28) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-3)e^2}{4\pi\varepsilon_o r_4^2} \mathbf{i}_r \tag{10.53}$$

for $r > r_3$.

In addition to the paramagnetic spin-pairing force between the third electron initially at radius r_3, the pairing causes the diamagnetic interaction between the outer electrons and the inner electrons given by Eq. (10.11) to vanish, except for an electrodynamic effect for $Z > 4$ described in the Two-Electron Atoms section, since upon pairing the magnetic field of the outer electrons becomes zero. Therefore, the force $\mathbf{F}_{mag\,2}$ is in the same direction as the spin-pairing force and is given by substitution of Eq. (7.4) with the radius r_4 into Eq. (10.5):

$$\mathbf{F}_{mag\,2} = \frac{\hbar e B}{2m_e r_1} = \frac{\mu_o e^2 \hbar^2}{2m_e^2 r_1 r_4^3}\mathbf{i}_r \tag{10.54}$$

Then, from Eqs. (10.54) and (7.6-7.15), the diamagnetic force is given by

$$\mathbf{F}_{mag\,2} = \frac{1}{Z}\frac{\hbar^2}{m_e r_1 r_4^2}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.55}$$

The outward centrifugal force on electron 4 is balanced by the electric force and the magnetic forces (on electron 4). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.53)), diamagnetic (Eqs. (10.11) and (10.35) for r_4), and paramagnetic (Eqs. (10.52) and (10.54)) forces as follows:

$$\frac{m_e v_4^2}{r_4} = \frac{(Z-3)e^2}{4\pi\varepsilon_o r_4^2} - \frac{\hbar^2}{4m_e r_4^2 r_1}\sqrt{s(s+1)} + \frac{\hbar^2}{Zm_e r_4^2 r_1}\sqrt{s(s+1)} - \left[\frac{Z-3}{Z-2}\right]\frac{r_1\hbar^2}{r_4^4 m_e}10\sqrt{s(s+1)} + \frac{\hbar^2}{Zm_e r_4^3}\sqrt{s(s+1)} \tag{10.56}$$

Substitution of $v_4 = \dfrac{\hbar}{m_e r_4}$ (Eq. (1.56) and $s = \dfrac{1}{2}$ into Eq. (10.56) gives:

$$\frac{\hbar^2}{m_e r_4^3} = \frac{(Z-3)e^2}{4\pi\varepsilon_o r_4^2} - \frac{\hbar^2}{4m_e r_4^2 r_1}\sqrt{\frac{3}{4}} + \frac{\hbar^2}{Zm_e r_4^2 r_1}\sqrt{\frac{3}{4}} - \left[\frac{Z-3}{Z-2}\right]\frac{r_1\hbar^2}{r_4^4 m_e}10\sqrt{\frac{3}{4}} + \frac{\hbar^2}{Zm_e r_4^3}\sqrt{\frac{3}{4}} \tag{10.57}$$

$$\left(\frac{(Z-3)e^2}{4\pi\varepsilon_o} - \left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\hbar^2}{m_e r_1}\sqrt{\frac{3}{4}}\right)\frac{1}{r_4^2} - \left[\frac{Z-3}{Z-2}\right]\frac{r_1\hbar^2}{r_4^4 m_e}10\sqrt{\frac{3}{4}} - \frac{\hbar^2}{m_e r_4^3}\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right) = 0 \tag{10.58}$$

The quadratic equation corresponding to Eq. (10.58) is

$$\left(\frac{(Z-3)e^2}{4\pi\varepsilon_o} - \left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\hbar^2}{m_e r_1}\sqrt{\frac{3}{4}}\right)r_4^2 - \frac{\hbar^2}{m_e}\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)r_4 - \left[\frac{Z-3}{Z-2}\right]\frac{r_1\hbar^2}{m_e}10\sqrt{\frac{3}{4}} = 0 \tag{10.59}$$

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$$r_4^2 - \frac{\frac{\hbar^2}{m_e}\left(1 - \frac{\sqrt{\frac{3}{4}}}{Z}\right)}{\frac{(Z-3)e^2}{4\pi\varepsilon_o} - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\hbar^2}{m_e r_1}\sqrt{\frac{3}{4}}} r_4 - \frac{\left[\frac{Z-3}{Z-2}\right]\frac{r_1\hbar^2}{m_e}10\sqrt{\frac{3}{4}}}{\frac{(Z-3)e^2}{4\pi\varepsilon_o} - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\hbar^2}{m_e r_1}\sqrt{\frac{3}{4}}} = 0 \quad (10.60)$$

$$r_4^2 - \frac{\left(1 - \frac{\sqrt{\frac{3}{4}}}{Z}\right)}{\frac{(Z-3)}{a_0} - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}} r_4 - \frac{\left[\frac{Z-3}{Z-2}\right]r_1 10\sqrt{\frac{3}{4}}}{\frac{(Z-3)}{a_0} - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}} = 0 \quad (10.61)$$

The solution of Eq. (10.61) using the quadratic formula is:

$$r_4 = r_3 = \frac{\frac{a_0\left(1 - \frac{\sqrt{\frac{3}{4}}}{Z}\right)}{(Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}} \pm a_0\sqrt{\frac{\left(1 - \frac{\sqrt{\frac{3}{4}}}{Z}\right)^2}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)^2} + 4\frac{\left[\frac{Z-3}{Z-2}\right]r_1 10\sqrt{\frac{3}{4}}}{(Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}}}}{2}$$

r_1 in units of a_0

$$(10.62)$$

where r_1 is given by Eq. (10.51) and also Eq. (7.19). The positive root of Eq. (10.62) must be taken in order that $r_4 > 0$. The final radius of electron 4, r_4, is given by Eq. (10.62); this is also the final radius of electron 3. The radii of several four-electron atoms are given in Table 10.2.

ENERGIES OF THE BERYLLIUM ATOM

The energy stored in the electric field, $E(electric)$, is given by Eq. (10.43) with the appropriate charge and radius:

$$E(electric) = -\frac{(Z-3)e^2}{8\pi\varepsilon_o r_4} \quad (10.63)$$

The ionization energy is given by the sum of the electric energy and the diamagnetic and paramagnetic energy terms. The magnetic energy, $E(magnetic)$, for an electron corresponding to a radius r_n given by Eq. (7.30) is

$$E(magnetic) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r_n^3}$$

(10.64)

Since there is no source of dissipative power, $\mathbf{J} \cdot \mathbf{E}$ of Eq. (10.27), to compensate for any potential change in the magnetic moments, Δm, of the inner electrons due to the ionization of an outer electron of the beryllium atom, there is a diamagnetic energy term in the ionization energy for this atom that follows from the corresponding term for the lithium atom. This term is given by Eqs. (10.15-10.24) wherein r_1 is given by Eq. (10.51) with $Z = 4$ and $r_3 = r_4$ is given by Eq. (10.62). Thus, the change in magnetic energy of the inner orbitsphere is $5.144\,\%$, so that the corresponding energy ΔE_{mag} is

$$\Delta E_{mag} = 0.05144 \; X \; 6.42291 \; eV = 0.33040 \; eV$$

(10.65)

where the magnetic energy of the inner electrons is $6.42291\,eV$. In addition, there is a paramagnetic energy term $E(magnetic)$ corresponding to the ionization of a spin-paired electron from a neutral atom with a closed s-shell. The energy follows from that given for helium by Eqs. (7.28) and (7.30) wherein the electron radius for helium is replaced by the radius r_4 of Eq. (10.62). Then, the ionization energy of the beryllium atom is given by Eqs. (7.28), (7.30), (10.25), and (10.62-10.65):

$$E(ionization;\; Be) = \frac{(Z-3)e^2}{8\pi\varepsilon_o r_4} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r_4^3} + \Delta E_{mag}$$

(10.66)

$$= 8.9216 \; eV + 0.03226 \; eV + 0.33040 \; eV = 9.28430 \; eV$$

The experimental ionization energy of beryllium is $9.32263\,eV$ [3].

THE IONIZATION ENERGIES OF FOUR-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>4

The ionization energies for the four-electron atoms with $Z > 4$ are given by the sum of the electric energy, $E(electric)$, given by Eq. (10.63) and the magnetic energies. The paramagnetic energy term corresponding to the ionization of a spin-paired electron from an atom with an external electric field is given by Eqs. (7.30) and (7.47) wherein the electron radius for helium is replaced by the radius r_4 of Eq. (10.62):

$$Ionization\; Energy = -Electric\; Energy - \frac{1}{Z} Magnetic\; Energy$$

(10.67)

Once the outer electrons of four-electron atoms with $Z > 4$ become spin unpaired during ionization, the corresponding magnetic field changes the velocities of the inner electrons in the same manner as shown for the case of the outer electron of three-electron atoms with $Z > 3$. The magnetic effect is calculated for the remaining electron 3 at the radius r_4 corresponding to condition of the derivation of Eq. (10.67) that follows from Eqs. (7.30) and (7.47). Thus, change in velocity, Δv, in the four-

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electron-atom case is that of three-electron atoms given by Eq. (10.46) wherein the electron radius r_3 is replaced by the radius r_4 of Eq. (10.62).

Since the velocities of electrons one and two decrease during ionization in the case of four-electron atoms rather than increase as in the case of three-electron atoms, the corresponding kinetic energy decreases and the kinetic energy term given by Eq. (10.47) is the opposite sign in Eq. (10.48).   Thus, the ionization energies of four-electron atoms with $Z > 4$ given by Eqs. (10.48) and (10.67) with the electric energy (Eq. (10.63)), the magnetic energy (Eq. (10.64)), and the change in the kinetic energy of the inner electrons (Eq. (10.47)) are

$$E(Ionization) = -Electric\ Energy - \frac{1}{Z} Magnetic\ Energy - E_T \qquad (10.68)$$

The ionization energies for several four-electron atoms are given in Table 10.2.   Since the radii, r_4, are greater than 10% of a_0 corresponding to a velocity of less than $1.5 \times 10^7\ m/s$, the relativistic corrections are negligible and are not included in Table 10.2.

Table 10.2.   Ionization energies for some four-electron atoms.

4 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	Electric Energy [c] (eV)	Magnetic Energy [d] (eV)	Δv [e] (m/s X 10^{-3})	ΔE_T [f] (eV)	Theoretical Ionization Energies [g] (eV)	Experimental Ionization Energies [h] (eV)	Relative Error [i]
Be	4	0.26116	1.52503	8.9178	0.03226	0.4207	0.0101	9.28430	9.32263	0.0041
B^+	5	0.20670	1.07930	25.2016	0.0910	0.7434	0.0314	25.1627	25.15484	-0.0003
C^{2+}	6	0.17113	0.84317	48.3886	0.1909	1.0688	0.0650	48.3125	47.8878	-0.0089
N^{3+}	7	0.14605	0.69385	78.4029	0.3425	1.3969	0.1109	78.2765	77.4735	-0.0104
O^{4+}	8	0.12739	0.59020	115.2148	0.5565	1.7269	0.1696	115.0249	113.899	-0.0099
F^{5+}	9	0.11297	0.51382	158.8102	0.8434	2.0582	0.2409	158.5434	157.1651	-0.0088
Ne^{6+}	10	0.10149	0.45511	209.1813	1.2138	2.3904	0.3249	208.8243	207.2759	-0.0075
Na^{7+}	11	0.09213	0.40853	266.3233	1.6781	2.7233	0.4217	265.8628	264.25	-0.0061
Mg^{8+}	12	0.08435	0.37065	330.2335	2.2469	3.0567	0.5312	329.6559	328.06	-0.0049
Al^{9+}	13	0.07778	0.33923	400.9097	2.9309	3.3905	0.6536	400.2017	398.75	-0.0036
Si^{10+}	14	0.07216	0.31274	478.3507	3.7404	3.7246	0.7888	477.4989	476.36	-0.0024
P^{11+}	15	0.06730	0.29010	562.5555	4.6861	4.0589	0.9367	561.5464	560.8	-0.0013
S^{12+}	16	0.06306	0.27053	653.5233	5.7784	4.3935	1.0975	652.3436	652.2	-0.0002
Cl^{13+}	17	0.05932	0.25344	751.2537	7.0280	4.7281	1.2710	749.8899	749.76	-0.0002
Ar^{14+}	18	0.05599	0.23839	855.7463	8.4454	5.0630	1.4574	854.1849	854.77	0.0007
K^{15+}	19	0.05302	0.22503	967.0007	10.0410	5.3979	1.6566	965.2283	968	0.0029
Ca^{16+}	20	0.05035	0.21308	1085.0167	11.8255	5.7329	1.8687	1083.0198	1087	0.0037
Sc^{17+}	21	0.04794	0.20235	1209.7940	13.8094	6.0680	2.0935	1207.5592	1213	0.0045
Ti^{18+}	22	0.04574	0.19264	1341.3326	16.0032	6.4032	2.3312	1338.8465	1346	0.0053
V^{19+}	23	0.04374	0.18383	1479.6323	18.4174	6.7384	2.5817	1476.8813	1486	0.0061
Cr^{20+}	24	0.04191	0.17579	1624.6929	21.0627	7.0737	2.8450	1621.6637	1634	0.0075
Mn^{21+}	25	0.04022	0.16842	1776.5144	23.9495	7.4091	3.1211	1773.1935	1788	0.0083
Fe^{22+}	26	0.03867	0.16165	1935.0968	27.0883	7.7444	3.4101	1931.4707	1950	0.0095
Co^{23+}	27	0.03723	0.15540	2100.4398	30.4898	8.0798	3.7118	2096.4952	2119	0.0106
Ni^{24+}	28	0.03589	0.14961	2272.5436	34.1644	8.4153	4.0264	2268.2669	2295	0.0116
Cu^{25+}	29	0.03465	0.14424	2451.4080	38.1228	8.7508	4.3539	2446.7858	2478	0.0126

[a] Radius of the paired inner electrons of four-electron atoms from Eq. (10.51).

[b] Radius of the paired outer electrons of four-electron atoms from Eq. (10.62).

[c] Electric energy of the outer electrons of four-electron atoms from Eq. (10.63).

[d] Magnetic energy of the outer electrons of four-electron atoms upon unpairing from Eq. (7.30) and Eq. (10.64).

[e] Change in the velocity of the paired inner electrons due to the unpaired outer electron of four-electron atoms during ionization from Eq. (10.46).

[f] Change in the kinetic energy of the paired inner electrons due to the unpaired outer electron of four-electron atoms during ionization from Eq. (10.47).

[g] Calculated ionization energies of four-electron atoms from Eq. (10.68) for $Z > 4$ and Eq. (10.66) for Be.

[h] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

[i] (Experimental-theoretical)/experimental.

.350 ;

The agreement between the experimental and calculated values of Table 10.2 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The beryllium atom isoelectronic series is given in Table 10.2 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of Be isoelectronic and Rydberg series, as well as direct experimental data.

2P-ORBITAL ELECTRONS BASED ON AN ENERGY MINIMUM

For each four-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)) and two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62). For $Z \geq 5$, the next electron which binds to form the corresponding five-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons such that it forms and unpaired orbitsphere at radius r_5.

The central Coulomb force, $\mathbf{F}_{ele}$, acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner four electrons is given by Eq. (10.28) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\varepsilon_o r_5^2}\mathbf{i}_r \qquad (10.69)$$

for $r > r_4$. The same form of force equation also applies to six through ten-electron atoms as well as five-electron atoms:

$$\mathbf{F}_{ele} = \frac{(Z-n)e^2}{4\pi\varepsilon_o r_n^2}\mathbf{i}_r \qquad (10.70)$$

for $r > r_{n-1}$ where n corresponds to the number of electrons of the atom and Z is its atomic number. In each case, the magnetic field of the binding outer electron changes the angular velocities of the inner electrons. However, in each case, the magnetic field of the outer electron provides a central Lorentzian force which exactly balances the change in centrifugal force because of the change in angular velocity [1]. The inner electrons remain at their initial radii, but cause a diamagnetic force

according to Lenz's law.

The diamagnetic force, $\mathbf{F}_{diamagnetic}$, for the formation of an s orbital given by Eq. (10.11) with the appropriate radii is

$$\mathbf{F}_{diamagnetic} = -\frac{\hbar^2}{4m_e r_n^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.71}$$

However, with the formation of a third shell, a nonuniform distribution of charge is possible that achieves an energy minimum. Minimum energy configurations are given by solutions to Laplace's Equation. The general form of the solution (Eq. (11.1)) is

$$\Phi(r,\theta,\phi) = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} B_{\ell,m} r^{-(\ell+1)} Y_\ell^m(\theta,\phi) \tag{10.72}$$

As shown in the Excited States of the One-Electron Atom (Quantization) section, this general solution in the form of a wave-equation gives the functions of the resonant photons of excited states. From Eqs. (2.15-2.16):

$$\mathbf{E}_{r\,photon\,n,l,m} = \frac{e(na_H)^\ell}{4\pi\varepsilon_o}\frac{1}{r^{(\ell+2)}}\left[-Y_0^0(\theta,\phi) + \frac{1}{n}\left[Y_0^0(\theta,\phi) + \mathrm{Re}\left\{Y_\ell^m(\theta,\phi)e^{i\omega_n t}\right\}\right]\right]\delta(r-r_n)$$
$$\omega_n = 0 \text{ for } m = 0 \tag{10.73}$$
$$n = 1,2,3,4,...$$
$$\mathbf{\ell} = 1,2,...,n-1$$
$$m = -\mathbf{\ell},-\mathbf{\ell}+1,...,0,...,+\mathbf{\ell}$$

$\mathbf{E}_{r\,total}$ is the sum of the "trapped photon" and proton electric fields,

$$\mathbf{E}_{r\,total} = \frac{e}{4\pi\varepsilon_o r^2} + \frac{e(na_H)^\ell}{4\pi\varepsilon_o}\frac{1}{r^{(\ell+2)}}\left[-Y_0^0(\theta,\phi) + \frac{1}{n}\left[Y_0^0(\theta,\phi) + \mathrm{Re}\left\{Y_\ell^m(\theta,\phi)e^{i\omega_n t}\right\}\right]\right]\delta(r-r_n)$$
$$\omega_n = 0 \text{ for } m = 0 \tag{10.74}$$

As shown in the Angular Function section and the Instability of Excited States section, the charge-density functions including the time-function factor are also solutions of Laplace's equation in the form of a wave-equation (Eqs. (1.48-1.49)):

$\mathbf{\ell} = 0$

$$\rho(r,\theta,\phi,t) = \frac{e}{8\pi r^2}[\delta(r-r_n)]\left[Y_0^0(\theta,\phi) + Y_\ell^m(\theta,\phi)\right] \tag{10.75}$$

$\mathbf{\ell} \neq 0$

$$\rho(r,\theta,\phi,t) = \frac{e}{4\pi r^2}[\delta(r-r_n)]\left[Y_0^0(\theta,\phi) + \mathrm{Re}\left\{Y_\ell^m(\theta,\phi)\left[1+e^{i\omega_n t}\right]\right\}\right] \tag{10.76}$$

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$$\rho(r,\theta,\phi,t) = \frac{e}{4\pi r^2}[\delta(r-r_n)]\left[Y_0^0(\theta,\phi) + \mathrm{Re}\{Y_\ell^m(\theta,\phi)e^{i\omega_n t}\}\right]$$ (10.77)

where

$$\mathrm{Re}\{Y_\ell^m(\theta,\phi)[1+e^{i\omega_n t}]\} = \mathrm{Re}[Y_\ell^m(\theta,\phi)+Y_\ell^m(\theta,\phi)e^{i\omega_n t}] = P_\ell^m(\cos\theta)\cos m\phi + P_\ell^m(\cos\theta)\cos(m\phi+\omega_n t)$$

or $\mathrm{Re}\{Y_\ell^m(\theta,\phi)e^{i\omega_n t}\} = P_\ell^m(\cos\theta)\cos(m\phi+\omega_n t)$ and to keep the form of the spherical harmonic as a traveling wave about the z-axis, $\omega_n = m\omega_n$. In the cases that $m \neq 0$, Eq. (1.65) is a traveling charge-density wave that moves on the surface of the orbitsphere about the z-axis with frequency ω_n and modulates the orbitsphere corresponding to $\ell = 0$. These functions comprise the well known s, p, d, f, etc. orbitals wherein the constant function $Y_0^0(\theta,\phi)$ corresponds to the spin function having spin angular momentum and the modulation function $\mathrm{Re}\{Y_\ell^m(\theta,\phi)e^{i\omega_n t}\}$ corresponds to the orbital function having orbital angular momentum as given in the Angular Function section and the Rotational Parameters of the Electron (Angular Momentum, Rotational Energy, Moment of Inertia) section.

Similar to the phenomenon observed for spherical conductors [4-5], spherical harmonic charge-density waves may be induced in the inner electron orbitspheres with the addition of one or more outer electrons, each having an orbital quantum number $\ell \neq 0$ as given by Eq. (10.77). With $Z > 5$, an energy minimum is achieved when the fifth through tenth electrons of each five through ten-electron atom fills a p orbital with the formation of orthogonal complementary charge-density waves in the inner shell electrons. To maintain the symmetry of the central charge and the energy minimum condition given by solutions to Laplace's equation (Eq. (10.72)), the charge-density waves on electron orbitspheres at r_1 and r_3 complement those of the outer orbitals when the outer p orbitals are not all occupied by at least one electron, and the complementary charge-density waves are provided by electrons at r_3 when this condition is met. Since the angular harmonic charge-density waves are nonradiative as shown in the Spacetime Fourier Transform of the Electron Function section and Appendix I: Nonradiation Based on the Electromagnetic Fields and the Poynting Power Vector, the time-averaged central field is inverse r-squared even though the central field is modulated by the concentric charge-density waves. The modulated central field maintains the spherical harmonic orbitals that maintain the spherical-harmonic phase according to Eq. (10.72). For $\ell = 1$ and $m = \pm 1$, the spherical harmonics $Y_\ell^m(\theta,\phi)$ given by Eqs. (1.66-1.67) are

$$Y_{1,x} = \sin\theta\cos\phi$$ (10.78)

$$Y_{1,y} = \sin\theta\sin\phi$$ (10.79)

wherein the x and y designation corresponds, respectively, to the historical p_x and p_y probability-density functions of quantum mechanics. The p_x and p_y charge-density waves rotate in the same direction such that their individual contributions to the diamagnetic force add, or they rotate in opposite directions such that their contributions cancel. In addition, for $\ell = 1$ and $m = 0$, the spherical harmonic $Y_\ell^m(\theta,\phi)$ is

$$Y_{1,z} = \cos\theta \tag{10.80}$$

wherein the z designation corresponds to the historical p_z probability-density function of quantum mechanics. The demonstration that the modulated orbitsphere solutions are solutions of the wave equation appears in Box 1.1.

As shown by Eq. (10.9), the diamagnetic force is dependent on the integral of the charge-density squared over the surface of the orbitsphere with the further constant of the invariance of charge under Gauss's integral law. The correction to the force due to a time and spatially-dependent spherical harmonic current-density wave is given by the normalization term for spherical harmonics given by Eq. (3.53) of Jackson [6] and Eq. (6-76) of McQuarrie [7]:

$$\frac{(\ell + |m|)!}{(2\ell + 1)(\ell - |m|)!} \tag{10.81}$$

Since the spin function is constant and the orbital function is a traveling wave, only the latter contributes to the diamagnetic and paramagnetic-force contributions of an unpaired electron. Substitution of Eq. (10.81) into Eq. (10.11) gives the contribution of each orbital to the diamagnetic force, $F_{diamagnetic}$, which is summed over the orbitals:

$$F_{diamagnetic} = -\sum_m \frac{(\ell + |m|)!}{(2\ell + 1)(\ell - |m|)!} \frac{\hbar^2}{4m_e r_n^2 r_3} \sqrt{s(s+1)}\mathbf{i}_r \tag{10.82}$$

where the contributions from orbitals having $|m| = 1$ add positively or negatively.

For each five-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), and an unpaired electron is in an orbitsphere at r_5 given by Eq. (10.113). For $Z \geq 6$, the next electron which binds to form the corresponding six-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons. A paramagnetic spin-paring force to form a filled s orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (7.15) with the radius r_6) reduces the energy of the atom

less than that due to the alternative forces on two unpaired p electrons in an orbitsphere at the same radius r_6.

In general, a nonuniform distribution of charge achieves an energy minimum with the formation of a third shell due to the dependence of the magnetic forces on the nuclear charge and orbital energy (Eqs. (10.52), (10.55), and (10.93)). The outer electrons of atoms and ions that are isoelectronic with the series boron through neon half-fill a 2p level with unpaired electrons at nitrogen, then fill the level with paired electrons at neon. *Thus, it is found that the purely postulated Hund's Rule and the Pauli Exclusion Principle of the assignment of unique quantum numbers to all electrons are not "weird spooky action" phenomena unique to quantum mechanics that require all electrons in the universe to have instantaneous communication and coordination with no basis in physical laws such as Maxwell's equations. Rather they are phenomenological consequences of those laws.*

Each outer 2p electron contributes spin as well as orbital angular momentum. The former gives rise to spin pairing to another 2p electron when an energy minimum is achieved. The corresponding force, $F_{mag\,2}$, given by Eq. (10.52) is:

$$F_{mag\,2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \tag{10.83}$$

The orbital angular momenta of spin-paired electrons may add to double the spin-pairing force of each individual p electron such that the resultant force is four times that of Eq. (10.83) in agreement with the energy (and force) relationship of magnetic fields (Eq. (1.122)):

$$F_{mag\,2} = \frac{1}{Z} \frac{4\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \tag{10.84}$$

Or, the orbital angular momenta of spin-paired electrons may add negatively to cancel such that $F_{mag\,2}$ due to the contribution from spin-pairing alone is equivalent to that given by Eq. (10.83).

Since the electron velocity given by Eq. (1.47) is

$$v_n = \frac{\hbar}{m_e r_n} \tag{10.85}$$

The scalar sum of the magnitude of the angular momentum of each infinitesimal point of the orbitsphere L_i of mass m_i must be constant. The constant is $\hbar$.

$$\sum |L_i| = \sum |\mathbf{r} \times m_i \mathbf{v}| = m_e r_n \frac{\hbar}{m_e r_n} = \hbar \tag{10.86}$$

where the velocity is given by Eq. (1.47). The sum of the magnitude of the angular momentum of the electron is $\hbar$ in any inertial frame and is relativistically invariant. The vector projections of the orbitsphere spin

angular momentum relative to the Cartesian coordinates are given in the Spin Angular Momentum of the Orbitsphere with $\ell = 0$ section.   The orbital and spin angular momentum of excited states is also quantized in units of $\hbar$ as shown in the Orbital and Spin Splitting section.   The orbital moment of inertia, $I_{orbital}$, corresponding to orbital quantum number ℓ (Eq. (1.96)) is

$$I_{orbital} = m_e r_n^2 \left[\frac{\ell(\ell+1)}{\ell^2 + 2\ell + 1} \right]^{\frac{1}{2}} = m_e r_n^2 \sqrt{\frac{\ell}{\ell+1}} \qquad (10.87)$$

The spin and orbital angular momentum can superimpose positively or negatively:

$$L_{z\,total} = L_{z\,spin} + L_{z\,orbital} \qquad (10.88)$$

Thus, the contribution of the orbital angular momentum to the paramagnetic force is also that given by Eq. (10.83):

$$\mathbf{F}_{mag\,2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \qquad (10.89)$$

And, the total force is given as the sum over the orbital and spin angular momenta that may add positively or negatively to achieve an energy minimum while maintaining the conservation of angular momentum.

The amplitude of the corresponding rotational energy, $E_{rotational\,orbital}$, given by Eqs. (1.95-1.96) is

$$E_{rotational\,orbital} = \frac{\hbar^2}{2m_e r_n^2} \left[\frac{\ell(\ell+1)}{\ell^2 + 2\ell + 1} \right]^{\frac{1}{2}} = \frac{\hbar^2}{2m_e r_n^2} \sqrt{\frac{\ell}{\ell+1}} \qquad (10.90)$$

Since the orbital rotational energy arises from a spin function (spin angular momentum) modulated by a spherical harmonic angular function (orbital angular momentum), the time-averaged orbital rotational energy having an amplitude given by Eq. (1.95) (Eq. (10.90)) is zero:

$$\langle E_{rotational\,orbital} \rangle = 0 \qquad (10.91)$$

However, the orbital energy is nonzero in the presence of a magnetic field.

N-electron atoms having $Z > n$ possess an electric field of

$$\mathbf{E} = \frac{(Z-n)e}{4\pi\varepsilon_o r^2} \mathbf{i}_r \qquad (10.92)$$

for $r > r_n$.   Since there is a source of dissipative, $\mathbf{J} \bullet \mathbf{E}$ of Eq. (10.27), the magnetic moments of the inner electrons may change due to the outer electron such that the energy of the n-electron atom is lowered.   The diamagnetic force, $\mathbf{F}_{diamagnetic\,2}$, due to a relativistic effect with an electric field for $r > r_n$ (Eq. (10.35)) is dependent on the amplitude of the orbital energy.   Using the orbital energy with $\ell = 1$ (Eq. (10.90)), the energy $m_e \Delta v^2$

.356 .

of Eq. (10.29) is reduced by the factor of $\left(1 - \frac{\sqrt{2}}{2}\right)$ due to the contribution of the charge-density wave of the inner electrons at r_3. Thus, $\mathbf{F}_{diamagnetic\,2}$ is given by

$$\mathbf{F}_{diamagnetic\,2} = -\left[\frac{Z-n}{Z-(n-1)}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3 \hbar^2}{m_e r_n^4} 10\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.93)$$

Using the forces given by Eqs. (10.70), (10.82-10.84), (10.89), (10.93), and the radii r_3 given by Eq. (10.62), the radii of the 2p electrons of all five through ten-electron atoms may be solved exactly. The electric energy given by Eq. (10.102) gives the corresponding exact ionization energies. $\mathbf{F}_{ele}$ and $\mathbf{F}_{diamagnetic\,2}$ given by Eqs. (10.70) and (10.93), respectively, are of the same form for all atoms with the appropriate nuclear charges and atomic radii. $\mathbf{F}_{diamagnetic}$ given by Eq. (10.82) and $\mathbf{F}_{mag\,2}$ given by Eqs. (10.83-10.84) and (10.89) are of the same form with the appropriate factors that depend on the minimum-energy electron configuration. The general equation and the summary of the parameters that determine the exact radii and ionization energies of all five through ten-electron atoms are given the General Equation For The Ionization Energies of Five Through Ten-Electron Atoms section and in Table 10.9.

FIVE-ELECTRON ATOMS

Five-electron atoms can be solved exactly using the results of the solutions of one, two, three, and four-electron atoms.

RADIUS AND IONIZATION ENERGY OF THE OUTER ELECTRON OF THE BORON ATOM

For each four-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)) and two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62). For $Z \geq 5$, the next electron which binds to form the corresponding five-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons such that it forms and unpaired orbitsphere at radius r_5. The resulting electron configuration is $1s^2 2s^2 2p^1$, and the orbital arrangement is

2p state

$$\underline{\uparrow} \quad \underline{} \quad \underline{} \qquad\qquad (10.94)$$
$$\;1 \qquad 0 \quad -1$$

corresponding to the ground state $^2P^0_{1/2}$.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner four electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\varepsilon_o r_5^2}\mathbf{i}_r \tag{10.95}$$

for $r > r_4$.

The single p orbital of the boron atom produces a diamagnetic force equivalent to that of the formation of an s orbital due to the induction of complementary and spherically symmetrical charge-density waves on electron orbitspheres at r_1 and r_3 in order to achieve a solution of Laplace's equation (Eq. (10.72)). The inner electrons remain at their initial radii, but cause a diamagnetic force according to Lenz's law that is two times that of Eqs. (10.11) and (10.71) since the two electrons at $r_1 = r_2$ act on the two electrons at $r_3 = r_4$ which in turn act of the outer electron. $\mathbf{F}_{diamagnetic}$ is also given by Eq. (10.82) with the appropriate radii when the contributions from the three orthogonal spherical harmonics are summed over including those induced:

$$\mathbf{F}_{diamagnetic} = -\frac{2\hbar^2}{4m_e r_5^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.96}$$

The charge induction forms complementary mirror charge-density waves which must have opposing angular momenta such that momentum is conserved. In this case, $\mathbf{F}_{mag\,2}$ given by Eq. (10.89) is zero:

$$\mathbf{F}_{mag\,2} = 0 \tag{10.97}$$

The outward centrifugal force on electron 5 is balanced by the electric force and the magnetic force (on electron 5). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.95)) and diamagnetic (Eq. (10.96)) forces as follows:

$$\frac{m_e v_5^2}{r_5} = \frac{(Z-4)e^2}{4\pi\varepsilon_o r_5^2} - \frac{2\hbar^2}{4m_e r_5^2 r_3}\sqrt{s(s+1)} \tag{10.98}$$

Substitution of $v_5 = \frac{\hbar}{m_e r_5}$ (Eq. (1.56)) and $s = \frac{1}{2}$ into Eq. (10.98) gives:

$$\frac{\hbar^2}{m_e r_5^3} = \frac{(Z-4)e^2}{4\pi\varepsilon_o r_5^2} - \frac{\hbar^2}{2m_e r_5^2 r_3}\sqrt{\frac{3}{4}} \tag{10.99}$$

$$r_5 = \frac{a_0}{\left((Z-4) - \frac{\sqrt{\frac{3}{4}}}{2r_3}\right)}, \quad r_3 \text{ in units of } a_0 \tag{10.100}$$

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Substitution of $\frac{r_3}{a_0} = 1.07930$ (Eq. (10.62) with $Z = 5$) into Eq. (10.100) gives

$$r_5 = 1.67000351a_0 \tag{10.101}$$

In general, the energy stored in the electric field, $E(electric)$, is given by Eq. (10.43) with the appropriate charge and radius:

$$E(electric) = -\frac{(Z - (n-1))e^2}{8\pi\varepsilon_o r_n} \tag{10.102}$$

where n corresponds to the number of electrons of the atom and Z is its atomic number.   The ionization energy is given by the sum of the electric energy and the energy corresponding to the change in magnetic-moments of the inner shell electrons.   Since there is no source of dissipative power, $\mathbf{J} \bullet \mathbf{E}$ of Eq. (10.27), to compensate for any potential change in the magnetic moments, Δm, of the inner electrons due to the ionization of the outer electron of the boron atom, there is a diamagnetic energy term in the ionization energy for this atom that follows from the corresponding term for the lithium atom.   Since the diamagnetic force for the boron atom (Eq. (10.96)) is twice that of the corresponding force (Eq. (10.11)) of the lithium atom, this term is given by twice that of Eqs. (10.15-10.24), with $Z = 5$, r_3 given by Eq. (10.62), and r_5 given by Eq. (10.101).   Thus, the change in magnetic energy of the inner orbitsphere at r_3 is 85.429321 %, so that the corresponding energy ΔE_{mag} is

$$\Delta E_{mag} = 2(0.85429321 \times 0.09100214 \ eV) = 0.15548501 \ eV \tag{10.103}$$

where the magnetic energy of the inner electrons is $0.09100214 \ eV$ (Eqs. (10.64) and (10.101)).   Then, the ionization energy of the boron atom is given by Eqs. (10.101-10.102) and (10.103):

$$E(ionization; \ B) = \frac{(Z-4)e^2}{8\pi\varepsilon_o r_5} + \Delta E_{mag} \tag{10.104}$$

$$= 8.147170901 \ eV + 0.15548501 \ eV = 8.30265592 \ eV$$

The experimental ionization energy of the boron atom is $8.29803 \ eV$ [3].

THE IONIZATION ENERGIES OF FIVE-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>5

Five-electron atoms having $Z > 5$ possess an external electric field given by Eq. (10.92).   In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that $\mathbf{F}_{diamagnetic}$ is minimized while $\mathbf{F}_{mag2}$ is maximized.   From Eq. (10.82), the diamagnetic force, $\mathbf{F}_{diamagnetic}$, is given by the sum of the contributions from the p_x, p_y, and p_z orbitals corresponding to $m = 1, -1$, and 0, respectively:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3} + \frac{2}{3} + \frac{1}{3}\right)\frac{\hbar^2}{4m_e r_5^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{5}{3}\right)\frac{\hbar^2}{4m_e r_5^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.105}$$

With $Z > 5$, the charge induction forms complementary mirror charge-density waves such that the angular momenta do not cancel. From Eq. (10.89), $\mathbf{F}_{mag\,2}$ corresponding to the orbital angular momentum of the single p_x electron is

$$\mathbf{F}_{mag\,2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_5^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \qquad (10.106)$$

The second diamagnetic force, $\mathbf{F}_{diamagnetic\,2}$, due to the binding of the p-orbital electron having an electric field outside of its radius is given by Eq. (10.93):

$$\mathbf{F}_{diamagnetic\,2} = -\left[\frac{Z-5}{Z-4}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3 \hbar^2}{m_e r_5^4} 10\sqrt{s(s+1)} \mathbf{i}_r \qquad (10.107)$$

In the case that $Z > 5$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.95)) and diamagnetic (Eqs. (10.105) and (10.107)), and paramagnetic (Eq. (10.106)) forces as follows:

$$\frac{m_e v_5^2}{r_5} = \frac{(Z-4)e^2}{4\pi\varepsilon_o r_5^2} - \frac{5\hbar^2}{12 m_e r_5^2 r_3}\sqrt{s(s+1)} + \frac{\hbar^2}{Z m_e r_5^2 r_3}\sqrt{s(s+1)} - \left[\frac{Z'-5}{Z-4}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3 \hbar^2}{r_5^4 m_e} 10\sqrt{s(s+1)} \qquad (10.108)$$

Substitution of $v_5 = \dfrac{\hbar}{m_e r_5}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.108) gives:

$$\frac{\hbar^2}{m_e r_5^3} = \frac{(Z-4)e^2}{4\pi\varepsilon_o r_5^2} - \frac{5\hbar^2}{12 m_e r_5^2 r_3}\sqrt{\frac{3}{4}} + \frac{\hbar^2}{Z m_e r_5^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-5}{Z-4}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3 \hbar^2}{r_5^4 m_e} 10\sqrt{\frac{3}{4}} \qquad (10.109)$$

The quadratic equation corresponding to Eq. (10.109) is

$$\left(\frac{(Z-4)e^2}{4\pi\varepsilon_o} - \left(\frac{5}{12} - \frac{1}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)r_5^2 - \frac{\hbar^2}{m_e}r_5 - \left[\frac{Z-5}{Z-4}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3 \hbar^2}{m_e} 10\sqrt{\frac{3}{4}} = 0 \qquad (10.110)$$

$$r_5^2 - \frac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-4)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{1}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)}r_5 - \frac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-5}{Z-4}\right]\left(1 - \dfrac{\sqrt{2}}{2}\right)r_3 10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-4)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{1}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)} = 0 \qquad (10.111)$$

The solution of Eq. (10.111) using the quadratic formula is:

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$$r_5 = \frac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-4)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{1}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)} \pm \sqrt{\left(\dfrac{\dfrac{\hbar^2}{m_e}}{\dfrac{(Z-4)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{1}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}}\right)^2 + 4\dfrac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-5}{Z-4}\right]\left(1 - \dfrac{\sqrt{2}}{2}\right)r_3 10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-4)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{1}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)}} \Bigg/ 2$$

(10.112)

$$r_5 = \frac{\dfrac{a_0}{\left((Z-4) - \left(\dfrac{5}{24} - \dfrac{1}{2Z}\right)\dfrac{\sqrt{3}}{r_3}\right)} \pm a_0 \sqrt{\left(\dfrac{1}{(Z-4) - \left(\dfrac{5}{24} - \dfrac{1}{2Z}\right)\dfrac{\sqrt{3}}{r_3}}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\dfrac{Z-5}{Z-4}\right]\left(1 - \dfrac{\sqrt{2}}{2}\right)r_3\right)}{(Z-4) - \left(\dfrac{5}{24} - \dfrac{1}{2Z}\right)\dfrac{\sqrt{3}}{r_3}}}}{2}$$

(10.113)

r_3 in units of a_0

where r_3 is given by Eq. (10.62). The positive root of Eq. (10.113) must be taken in order that $r_5 > 0$. The radii of several five-electron atoms are given in Table 10.3.

The ionization energies for the five-electron atoms with $Z > 5$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii, r_5, given by Eq. (10.113)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-4)e^2}{8\pi\varepsilon_o r_5}$$

(10.114)

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured five-electron atoms are given in Table 10.3.

Table 10.3. Ionization energies for some five-electron atoms.

5 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_5 (a_o) [c]	Theoretical Ionization Energies [d] (eV)	Experimental Ionization Energies [e] (eV)	Relative Error [f]
B	5	0.20670	1.07930	1.67000	8.30266	8.29803	-0.00056
C^+	6	0.17113	0.84317	1.12092	24.2762	24.38332	0.0044
N^{2+}	7	0.14605	0.69385	0.87858	46.4585	47.44924	0.0209
O^{3+}	8	0.12739	0.59020	0.71784	75.8154	77.41353	0.0206
F^{4+}	9	0.11297	0.51382	0.60636	112.1922	114.2428	0.0179
Ne^{5+}	10	0.10149	0.45511	0.52486	155.5373	157.93	0.0152
Na^{6+}	11	0.09213	0.40853	0.46272	205.8266	208.5	0.0128
Mg^{7+}	12	0.08435	0.37065	0.41379	263.0469	265.96	0.0110
Al^{8+}	13	0.07778	0.33923	0.37425	327.1901	330.13	0.0089
Si^{9+}	14	0.07216	0.31274	0.34164	398.2509	401.37	0.0078
P^{10+}	15	0.06730	0.29010	0.31427	476.2258	479.46	0.0067
S^{11+}	16	0.06306	0.27053	0.29097	561.1123	564.44	0.0059
Cl^{12+}	17	0.05932	0.25344	0.27090	652.9086	656.71	0.0058
Ar^{13+}	18	0.05599	0.23839	0.25343	751.6132	755.74	0.0055
K^{14+}	19	0.05302	0.22503	0.23808	857.2251	861.1	0.0045
Ca^{15+}	20	0.05035	0.21308	0.22448	969.7435	974	0.0044
Sc^{16+}	21	0.04794	0.20235	0.21236	1089.1678	1094	0.0044
Ti^{17+}	22	0.04574	0.19264	0.20148	1215.4975	1221	0.0045
V^{18+}	23	0.04374	0.18383	0.19167	1348.7321	1355	0.0046
Cr^{19+}	24	0.04191	0.17579	0.18277	1488.8713	1496	0.0048
Mn^{20+}	25	0.04022	0.16842	0.17466	1635.9148	1644	0.0049
Fe^{21+}	26	0.03867	0.16165	0.16724	1789.8624	1799	0.0051
Co^{22+}	27	0.03723	0.15540	0.16042	1950.7139	1962	0.0058
Ni^{23+}	28	0.03589	0.14961	0.15414	2118.4690	2131	0.0059
Cu^{24+}	29	0.03465	0.14424	0.14833	2293.1278	2308	0.0064

[a] Radius of the first set of paired inner electrons of five-electron atoms from Eq. (10.51).

[b] Radius of the second set of paired inner electrons of five-electron atoms from Eq. (10.62).

[c] Radius of the outer electron of five-electron atoms from Eq. (10.113) for $Z > 5$ and Eq. (10.101) for B.

[d] Calculated ionization energies of five-electron atoms given by the electric energy (Eq. (10.114)) for $Z > 5$ and Eq. (10.104) for B.

[e] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

[f] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.3 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray

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spectroscopy.   In this case, the experimental capability is three to four significant figures which is consistent with the last column.   The boron atom isoelectronic series is given in Table 10.3 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of B isoelectronic and Rydberg series, as well as direct experimental data.

SIX-ELECTRON ATOMS

Six-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, and five-electron atoms.

RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE CARBON ATOM

For each five-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), and an unpaired electron is in an orbitsphere at r_5 given by Eq. (10.113).   For $Z \geq 6$, the next electron which binds to form the corresponding six-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons.   A paramagnetic spin-paring force to form a filled s orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (7.15) with the radius r_6) reduces the energy of the atom less than that due to the alternative forces on two unpaired p electrons in an orbitsphere at the same radius r_6.   The resulting electron configuration is $1s^2 2s^2 2p^2$, and the orbital arrangement is

2p state

$$\underline{\uparrow} \quad \underline{\uparrow} \quad \underline{} \qquad \qquad (10.115)$$
$$\ \ 1 \qquad 0 \qquad -1$$

corresponding to the ground state $^3P_0$.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_o r_6^2} \mathbf{i}_r \qquad \qquad (10.116)$$

for $r > r_5$.

The two orthogonal electrons form charge-density waves such that the total angular momentum of the two outer electrons is conserved which determines the diamagnetic force according to Eq. (10.82). $\mathbf{F}_{diamagnetic}$ is

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right)\frac{\hbar^2}{4m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.117)$$

corresponding to $m = 1$.

The charge induction forms complementary mirror charge-density waves which must have opposing angular momenta such that momentum is conserved. In this case, $\mathbf{F}_{mag\,2}$ given by Eq. (10.89) is zero:

$$\mathbf{F}_{mag\,2} = 0 \qquad (10.118)$$

The outward centrifugal force on electron 6 is balanced by the electric force and the magnetic forces (on electron 6). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.116)) and diamagnetic (Eq. (10.117)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \frac{(Z-5)e^2}{4\pi\varepsilon_o r_6^2} - \frac{\hbar^2}{6m_e r_6^2 r_3}\sqrt{s(s+1)} \qquad (10.119)$$

Substitution of $v_6 = \dfrac{\hbar}{m_e r_6}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.119) gives:

$$\frac{\hbar^2}{m_e r_6^3} = \frac{(Z-5)e^2}{4\pi\varepsilon_o r_6^2} - \frac{\hbar^2}{6m_e r_6^2 r_3}\sqrt{\frac{3}{4}} \qquad (10.120)$$

$$r_6 = \frac{a_0}{\left((Z-5) - \dfrac{\sqrt{\dfrac{3}{4}}}{6r_3}\right)}, \; r_3 \text{ in units of } a_0 \qquad (10.121)$$

Substitution of $\dfrac{r_3}{a_0} = 0.84317$ (Eq. (10.62) with $Z = 6$) into Eq. (10.121) gives

$$r_6 = 1.20654a_0 \qquad (10.122)$$

The ionization energy of the carbon atom is given by the electric energy, $E(electric)$, (Eq. (10.102) with the radius, r_6, given by Eq. (10.122)):

$$E(ionization;\ C) = -Electric\ Energy = \frac{(Z-5)e^2}{8\pi\varepsilon_o r_6} = 11.27671\ eV \qquad (10.123)$$

where $r_6 = 1.20654a_0$ (Eq. (10.122)) and $Z = 6$. The experimental ionization energy of the carbon atom is $11.2603\ eV$ [3].

THE IONIZATION ENERGIES OF SIX-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>6

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Six-electron atoms having $Z > 6$ possess an external electric field given by Eq. (10.92). In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that $\mathbf{F}_{diamagnetic}$ is minimized while $\mathbf{F}_{mag\,2}$ is maximized. From Eq. (10.82), the diamagnetic force, $\mathbf{F}_{diamagnetic}$, is given by the sum of the contributions from the p_x, p_y, and p_z orbitals corresponding to $m = 1, -1,$ and 0, respectively:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3} + \frac{2}{3} + \frac{1}{3}\right)\frac{\hbar^2}{4m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{5}{3}\right)\frac{\hbar^2}{4m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.124)$$

With $Z > 6$, the charge induction forms complementary mirror charge-density waves such that the angular momenta do not cancel. From Eq. (10.89), $\mathbf{F}_{mag\,2}$ corresponding to the orbital angular momentum of the two p electrons in addition to complementary charge-density waves is

$$\mathbf{F}_{mag\,2} = 2\frac{1}{Z}\frac{2\hbar^2}{m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{4\hbar^2}{m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.125)$$

The second diamagnetic force, $\mathbf{F}_{diamagnetic\,2}$, due to the binding of the p-orbital electron having an electric field outside of its radius is given by Eq. (10.93):

$$\mathbf{F}_{diamagnetic\,2} = -\left[\frac{Z-6}{Z-5}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_6^4}10\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.126)$$

In the case that $Z > 6$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.116)), diamagnetic (Eqs. (10.124) and (10.126)), and paramagnetic (Eq. (10.125)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \frac{(Z-5)e^2}{4\pi\varepsilon_o r_6^2} - \frac{5\hbar^2}{12m_e r_6^2 r_3}\sqrt{s(s+1)} + \frac{4\hbar^2}{Zm_e r_6^2 r_3}\sqrt{s(s+1)} - \left[\frac{Z-6}{Z-5}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_6^4}10\sqrt{s(s+1)} \qquad (10.127)$$

Substitution of $v_6 = \dfrac{\hbar}{m_e r_6}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.127) gives:

$$\frac{\hbar^2}{m_e r_6^3} = \frac{(Z-5)e^2}{4\pi\varepsilon_o r_6^2} - \frac{5\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}} + \frac{4\hbar^2}{Zm_e r_6^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{\frac{3}{4}} \qquad (10.128)$$

The quadratic equation corresponding to Eq. (10.128) is

$$\left(\frac{(Z-5)e^2}{4\pi\varepsilon_o} - \left(\frac{5}{12} - \frac{4}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)r_6^2 - \frac{\hbar^2}{m_e}r_6 - \left[\frac{Z-6}{Z-5}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e}10\sqrt{\frac{3}{4}} = 0 \qquad (10.129)$$

$$r_6^2 - \cfrac{\cfrac{\hbar^2}{m_e}}{\left(\cfrac{(Z-5)e^2}{4\pi\varepsilon_o} - \left(\cfrac{5}{12} - \cfrac{4}{Z}\right)\cfrac{\hbar^2}{m_e r_3}\sqrt{\cfrac{3}{4}}\right)} r_6 - \cfrac{\cfrac{\hbar^2}{m_e}\left[\cfrac{Z-6}{Z-5}\right]\left(1 - \cfrac{\sqrt{2}}{2}\right)r_3 10\sqrt{\cfrac{3}{4}}}{\left(\cfrac{(Z-5)e^2}{4\pi\varepsilon_o} - \left(\cfrac{5}{12} - \cfrac{4}{Z}\right)\cfrac{\hbar^2}{m_e r_3}\sqrt{\cfrac{3}{4}}\right)} = 0$$

$$(10.130)$$

The solution of Eq. (10.130) using the quadratic formula is:

$$r_6 = \cfrac{\cfrac{\cfrac{\hbar^2}{m_e}}{\left(\cfrac{(Z-5)e^2}{4\pi\varepsilon_o} - \left(\cfrac{5}{12} - \cfrac{4}{Z}\right)\cfrac{\hbar^2}{m_e r_3}\sqrt{\cfrac{3}{4}}\right)} \pm \sqrt{\left(\cfrac{\cfrac{\hbar^2}{m_e}}{\left(\cfrac{(Z-5)e^2}{4\pi\varepsilon_o} - \left(\cfrac{5}{12} - \cfrac{4}{Z}\right)\cfrac{\hbar^2}{m_e r_3}\sqrt{\cfrac{3}{4}}\right)}\right)^2 + 4\cfrac{\cfrac{\hbar^2}{m_e}\left[\cfrac{Z-6}{Z-5}\right]\left(1 - \cfrac{\sqrt{2}}{2}\right)r_3 10\sqrt{\cfrac{3}{4}}}{\left(\cfrac{(Z-5)e^2}{4\pi\varepsilon_o} - \left(\cfrac{5}{12} - \cfrac{4}{Z}\right)\cfrac{\hbar^2}{m_e r_3}\sqrt{\cfrac{3}{4}}\right)}}}{2}$$

$$(10.131)$$

$$r_6 = \cfrac{\cfrac{a_0}{\left((Z-5) - \left(\cfrac{5}{24} - \cfrac{2}{Z}\right)\cfrac{\sqrt{3}}{r_3}\right)} \pm a_0\sqrt{\left(\cfrac{1}{\left((Z-5) - \left(\cfrac{5}{24} - \cfrac{2}{Z}\right)\cfrac{\sqrt{3}}{r_3}\right)}\right)^2 + \cfrac{20\sqrt{3}\left(\left[\cfrac{Z-6}{Z-5}\right]\left(1 - \cfrac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-5) - \left(\cfrac{5}{24} - \cfrac{2}{Z}\right)\cfrac{\sqrt{3}}{r_3}\right)}}}{2}$$

$$(10.132)$$

r_3 in units of a_0

where r_3 is given by Eq. (10.62). The positive root of Eq. (10.132) must be taken in order that $r_6 > 0$. The final radius of electron 6, r_6, is given by Eq. (10.132); this is also the final radius of electron 5. The radii of several six-electron atoms are given in Table 10.4.

The ionization energies for the six-electron atoms with $Z > 6$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii r_6, given by Eq. (10.132)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-5)e^2}{8\pi\varepsilon_o r_6} \qquad (10.133)$$

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured six-electron atoms are given in

Table 10.4.

Table 10.4.   Ionization energies for some six-electron atoms.

6 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_6 (a_o) [c]	Theoretical Ionization Energies [d] (eV)	Experimental Ionization Energies [e] (eV)	Relative Error [f]
C	6	0.17113	0.84317	1.20654	11.27671	11.2603	-0.0015
N^+	7	0.14605	0.69385	0.90119	30.1950	29.6013	-0.0201
O^{2+}	8	0.12739	0.59020	0.74776	54.5863	54.9355	0.0064
F^{3+}	9	0.11297	0.51382	0.63032	86.3423	87.1398	0.0092
Ne^{4+}	10	0.10149	0.45511	0.54337	125.1986	126.21	0.0080
Na^{5+}	11	0.09213	0.40853	0.47720	171.0695	172.18	0.0064
Mg^{6+}	12	0.08435	0.37065	0.42534	223.9147	225.02	0.0049
Al^{7+}	13	0.07778	0.33923	0.38365	283.7121	284.66	0.0033
Si^{8+}	14	0.07216	0.31274	0.34942	350.4480	351.12	0.0019
P^{9+}	15	0.06730	0.29010	0.32081	424.1135	424.4	0.0007
S^{10+}	16	0.06306	0.27053	0.29654	504.7024	504.8	0.0002
Cl^{11+}	17	0.05932	0.25344	0.27570	592.2103	591.99	-0.0004
Ar^{12+}	18	0.05599	0.23839	0.25760	686.6340	686.1	-0.0008
K^{13+}	19	0.05302	0.22503	0.24174	787.9710	786.6	-0.0017
Ca^{14+}	20	0.05035	0.21308	0.22772	896.2196	894.5	-0.0019
Sc^{15+}	21	0.04794	0.20235	0.21524	1011.3782	1009	-0.0024
Ti^{16+}	22	0.04574	0.19264	0.20407	1133.4456	1131	-0.0022
V^{17+}	23	0.04374	0.18383	0.19400	1262.4210	1260	-0.0019
Cr^{18+}	24	0.04191	0.17579	0.18487	1398.3036	1396	-0.0017
Mn^{19+}	25	0.04022	0.16842	0.17657	1541.0927	1539	-0.0014
Fe^{20+}	26	0.03867	0.16165	0.16899	1690.7878	1689	-0.0011
Co^{21+}	27	0.03723	0.15540	0.16203	1847.3885	1846	-0.0008
Ni^{22+}	28	0.03589	0.14961	0.15562	2010.8944	2011	0.0001
Cu^{23+}	29	0.03465	0.14424	0.14970	2181.3053	2182	0.0003

[a] Radius of the first set of paired inner electrons of six-electron atoms from Eq. (10.51).
[b] Radius of the second set of paired inner electrons of six-electron atoms from Eq. (10.62).
[c] Radius of the two unpaired outer electrons of six-electron atoms from Eq. (10.132) for $Z > 6$ and Eq. (10.122) for C.
[d] Calculated ionization energies of six-electron atoms given by the electric energy (Eq. (10.133)).
[e] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].
[f] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.4 is well within the experimental capability of the spectroscopic

determinations including the values at large Z which relies on X-ray spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The carbon atom isoelectronic series is given in Table 10.4 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of C isoelectronic and Rydberg series, as well as direct experimental data.

SEVEN-ELECTRON ATOMS

Seven-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, and six-electron atoms.

RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE NITROGEN ATOM

For each six-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), and two unpaired electrons is in an orbitsphere at r_5 given by Eq. (10.132). For $Z \geq 7$, the next electron which binds to form the corresponding seven-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons. A paramagnetic spin-paring force is also possible, but the force due to the spin-pairing of the electrons (Eq. (7.15) with the radius r_7) reduces the energy of the atom less than that due to the alternative forces on three unpaired p electrons in an orbitsphere at the same radius r_7. The resulting electron configuration is $1s^2 2s^2 2p^3$, and the orbital arrangement is

2p state

$$\underline{\uparrow} \quad \underline{\uparrow} \quad \underline{\uparrow} \qquad\qquad\qquad (10.134)$$

1   0   -1

corresponding to the ground state $^4S^0_{3/2}$.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner six electrons is given by Eq. (10.70) with the appropriate charge and radius:

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$$\mathbf{F}_{ele} = \frac{(Z-6)e^2}{4\pi\varepsilon_o r_7^2}\mathbf{i}_r \tag{10.135}$$

for $r > r_6$.

The energy is minimized with conservation of angular momentum when the angular momenta of the two orthogonal p_x and p_y electrons cancel such that the diamagnetic force (Eq. (10.82)), $\mathbf{F}_{diamagnetic}$, is

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_7^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.136}$$

corresponding to $m = 0$.

From Eq. (10.89), $\mathbf{F}_{mag\,2}$ corresponding to the orbital angular momentum of the p_z electron is

$$\mathbf{F}_{mag\,2} = \frac{1}{Z}\frac{\hbar^2}{m_e r_7^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.137}$$

The outward centrifugal force on electron 7 is balanced by the electric force and the magnetic forces (on electron 7). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.135)), diamagnetic (Eq. (10.136)), and paramagnetic (Eq. (10.137)) forces as follows:

$$\frac{m_e v_7^2}{r_7} = \frac{(Z-6)e^2}{4\pi\varepsilon_o r_7^2} - \frac{\hbar^2}{12m_e r_7^2 r_3}\sqrt{s(s+1)} + \frac{\hbar^2}{Z m_e r_7^2 r_3}\sqrt{s(s+1)} \tag{10.138}$$

Substitution of $v_7 = \dfrac{\hbar}{m_e r_7}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.138) gives:

$$\frac{\hbar^2}{m_e r_7^3} = \frac{(Z-6)e^2}{4\pi\varepsilon_o r_7^2} - \frac{\hbar^2}{12m_e r_7^2 r_3}\sqrt{\frac{3}{4}} + \frac{\hbar^2}{Z m_e r_7^2 r_3}\sqrt{\frac{3}{4}} \tag{10.139}$$

$$r_7 = \frac{\dfrac{\hbar^2}{m_e}}{\dfrac{(Z-6)e^2}{4\pi\varepsilon_o} - \dfrac{\hbar^2}{12m_e r_3}\sqrt{\dfrac{3}{4}} + \dfrac{\hbar^2}{Z m_e r_3}\sqrt{\dfrac{3}{4}}} \tag{10.140}$$

$$r_7 = \frac{a_0}{(Z-6) - \left(\dfrac{1}{12} - \dfrac{1}{Z}\right)\dfrac{\sqrt{\dfrac{3}{4}}}{r_3}}, \quad r_3 \text{ in units of } a_0 \tag{10.141}$$

Substitution of $\dfrac{r_3}{a_0} = 0.69385$ (Eq. (10.62) with $Z = 7$) into Eq. (10.141) gives

$$r_7 = 0.93084 a_0 \tag{10.142}$$

The ionization energy of the nitrogen atom is given by the electric energy, $E(electric)$, (Eq. (10.102) with the radius, r_7, given by Eq. (10.142)):

$$E(ionization;\ N) = -Electric\ Energy = \frac{(Z-6)e^2}{8\pi\varepsilon_o r_7} = 14.61664\ eV \tag{10.143}$$

where $r_7 = 0.93084a_0$ (Eq. (10.142)) and $Z = 7$. The experimental ionization energy of the nitrogen atom is $14.53414\,eV$ [3].

THE IONIZATION ENERGIES OF SEVEN-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>7

Seven-electron atoms having $Z > 7$ possess an external electric field given by Eq. (10.92). In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that $\mathbf{F}_{diamagnetic}$ is minimized while $\mathbf{F}_{mag\,2}$ is maximized. From Eq. (10.82), the diamagnetic force, $\mathbf{F}_{diamagnetic}$, is given by the sum of the contributions from the p_x, p_y, and p_z orbitals corresponding to $m = 1$, -1, and 0, respectively:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3} + \frac{2}{3} + \frac{1}{3}\right)\frac{\hbar^2}{4m_e r_7^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{5}{3}\right)\frac{\hbar^2}{4m_e r_7^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.144)$$

With $Z > 6$, the charge induction forms complementary mirror charge-density waves such that the angular momenta do not cancel. From Eq. (10.89), $\mathbf{F}_{mag\,2}$ corresponding to the orbital angular momentum of the three p electrons in addition complementary charge-density waves is

$$\mathbf{F}_{mag\,2} = 2\frac{1}{Z}\frac{3\hbar^2}{m_e r_7^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.145)$$

The second diamagnetic force, $\mathbf{F}_{diamagnetic\,2}$, due to the binding of the p-orbital electron having an electric field outside of its radius is given by Eq. (10.93):

$$\mathbf{F}_{diamagnetic\,2} = -\left[\frac{Z-7}{Z-6}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_7^4}10\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.146)$$

In the case that $Z > 7$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.135)), diamagnetic (Eqs. (10.10.144) and (10.146)), and paramagnetic (Eq. (10.145)) forces as follows:

$$\frac{m_e v_7^2}{r_7} = \frac{(Z-6)e^2}{4\pi\varepsilon_o r_7^2} - \frac{5\hbar^2}{12m_e r_7^2 r_3}\sqrt{s(s+1)} + \frac{6\hbar^2}{Zm_e r_7^2 r_3}\sqrt{s(s+1)} - \left[\frac{Z-7}{Z-6}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_7^4}10\sqrt{s(s+1)} \qquad (10.147)$$

Substitution of $v_7 = \frac{\hbar}{m_e r_7}$ (Eq. (1.56)) and $s = \frac{1}{2}$ into Eq. (10.147) gives:

$$\frac{\hbar^2}{m_e r_7^3} = \frac{(Z-6)e^2}{4\pi\varepsilon_o r_7^2} - \frac{5\hbar^2}{12m_e r_7^2 r_3}\sqrt{\frac{3}{4}} + \frac{6\hbar^2}{Zm_e r_7^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-7}{Z-6}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_7^4 m_e}10\sqrt{\frac{3}{4}} \qquad (10.148)$$

The quadratic equation corresponding to Eq. (10.148) is

$$\left(\frac{(Z-6)e^2}{4\pi\varepsilon_o} - \left(\frac{5}{12} - \frac{6}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)r_7^2 - \frac{\hbar^2}{m_e}r_7 - \left[\frac{Z-7}{Z-6}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e}10\sqrt{\frac{3}{4}} = 0$$

(10.149)

$$r_7^2 - \frac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-6)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)}r_7 - \frac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-7}{Z-6}\right]\left(1 - \dfrac{\sqrt{2}}{2}\right)r_3 10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-6)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)} = 0$$

(10.150)

The solution of Eq. (10.150) using the quadratic formula is:

$$r_7 = \frac{\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-6)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)} \pm \sqrt{\left(\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-6)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)}\right)^2 + 4\dfrac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-7}{Z-6}\right]\left(1 - \dfrac{\sqrt{2}}{2}\right)r_3 10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-6)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)}}}{2}$$

(10.151)

$$r_7 = \frac{\dfrac{a_0}{\left((Z-6) - \left(\dfrac{5}{24} - \dfrac{3}{Z}\right)\dfrac{\sqrt{3}}{r_3}\right)} \pm a_0 \sqrt{\left(\dfrac{1}{\left((Z-6) - \left(\dfrac{5}{24} - \dfrac{3}{Z}\right)\dfrac{\sqrt{3}}{r_3}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\dfrac{Z-7}{Z-6}\right]\left(1 - \dfrac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-6) - \left(\dfrac{5}{24} - \dfrac{3}{Z}\right)\dfrac{\sqrt{3}}{r_3}\right)}}}{2}$$

(10.152)

$$r_3 \text{ in units of } a_0$$

where r_3 is given by Eq. (10.62). The positive root of Eq. (10.152) must be taken in order that $r_7 > 0$. The final radius of electron 7, r_7, is given by Eq. (10.152); this is also the final radius of electrons 5 and 6. The radii of several seven-electron atoms are given in Table 10.5.

   The ionization energies for the seven-electron atoms with $Z > 7$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii, r_7, given by Eq. (10.152)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-6)e^2}{8\pi\varepsilon_o r_7}$$

(10.153)

Since the relativistic corrections were small, the nonrelativistic ionization

energies for experimentally measured seven-electron atoms are given in Table 10.5.

Table 10.5. Ionization energies for some seven-electron atoms.

7 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_7 (a_o) [c]	Theoretical Ionization Energies [d] (eV)	Experimental Ionization Energies [e] (eV)	Relative Error [f]
N	7	0.14605	0.69385	0.93084	14.61664	14.53414	-0.0057
O^+	8	0.12739	0.59020	0.78489	34.6694	35.1173	0.0128
F^{2+}	9	0.11297	0.51382	0.67084	60.8448	62.7084	0.0297
Ne^{3+}	10	0.10149	0.45511	0.57574	94.5279	97.12	0.0267
Na^{4+}	11	0.09213	0.40853	0.50250	135.3798	138.4	0.0218
Mg^{5+}	12	0.08435	0.37065	0.44539	183.2888	186.76	0.0186
Al^{6+}	13	0.07778	0.33923	0.39983	238.2017	241.76	0.0147
Si^{7+}	14	0.07216	0.31274	0.36271	300.0883	303.54	0.0114
P^{8+}	15	0.06730	0.29010	0.33191	368.9298	372.13	0.0086
S^{9+}	16	0.06306	0.27053	0.30595	444.7137	447.5	0.0062
Cl^{10+}	17	0.05932	0.25344	0.28376	527.4312	529.28	0.0035
Ar^{11+}	18	0.05599	0.23839	0.26459	617.0761	618.26	0.0019
K^{12+}	19	0.05302	0.22503	0.24785	713.6436	714.6	0.0013
Ca^{13+}	20	0.05035	0.21308	0.23311	817.1303	817.6	0.0006
Sc^{14+}	21	0.04794	0.20235	0.22003	927.5333	927.5	0.0000
Ti^{15+}	22	0.04574	0.19264	0.20835	1044.8504	1044	-0.0008
V^{16+}	23	0.04374	0.18383	0.19785	1169.0800	1168	-0.0009
Cr^{17+}	24	0.04191	0.17579	0.18836	1300.2206	1299	-0.0009
Mn^{18+}	25	0.04022	0.16842	0.17974	1438.2710	1437	-0.0009
Fe^{19+}	26	0.03867	0.16165	0.17187	1583.2303	1582	-0.0008
Co^{20+}	27	0.03723	0.15540	0.16467	1735.0978	1735	-0.0001
Ni^{21+}	28	0.03589	0.14961	0.15805	1893.8726	1894	0.0001
Cu^{22+}	29	0.03465	0.14424	0.15194	2059.5543	2060	0.0002

[a] Radius of the first set of paired inner electrons of seven-electron atoms from Eq. (10.51).
[b] Radius of the second set of paired inner electrons of seven-electron atoms from Eq. (10.62).
[c] Radius of the three unpaired paired outer electrons of seven-electron atoms from Eq. (10.152) for $Z > 7$ and Eq. (10.142) for N.
[d] Calculated ionization energies of seven-electron atoms given by the electric energy (Eq. (10.153)).
[e] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].
[f] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.5 is well within the experimental capability of the spectroscopic

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determinations including the values at large Z which relies on X-ray spectroscopy.   In this case, the experimental capability is three to four significant figures which is consistent with the last column.   The nitrogen atom isoelectronic series is given in Table 10.5 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of N isoelectronic and Rydberg series, as well as direct experimental data.

EIGHT-ELECTRON ATOMS

Eight-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, and seven-electron atoms.

RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE OXYGEN ATOM

For each seven-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), and three unpaired electrons is in an orbitsphere at r_7 given by Eq. (10.152). For $Z \geq 8$, the next electron which binds to form the corresponding eight-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons.   A paramagnetic spin-paring force that results in the formation of a filled s orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (7.15) with the radius r_8) reduces the energy of the atom less than that due to the alternative forces on two paired electrons in a p_x orbital and two unpaired electrons in p_z and p_z orbitals of an orbitsphere at the same radius r_8.   The resulting electron configuration is $1s^2 2s^2 2p^4$, and the orbital arrangement is

2p state ·

$$\underline{\uparrow \downarrow} \quad \underline{\uparrow} \quad \underline{\uparrow} \qquad\qquad (10.154)$$

$$\quad 1 \qquad 0 \qquad -1$$

corresponding to the ground state $^3P_2$.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner seven electrons is given by Eq. (10.70) with the

appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-7)e^2}{4\pi\varepsilon_o r_8^2}\mathbf{i}_r \tag{10.155}$$

for $r > r_7$.

The energy is minimized with conservation of angular momentum by the cancellation of the orbital angular momentum of a p_x electron by that of the p_y electron with the pairing of electron eight to fill the p_x orbital. Then, the diamagnetic force is that of N given by Eq. (10.136) corresponding to the p_z-orbital electron (Eq. (10.82) with $m = 0$) as the source of diamagnetism with an additional contribution from the uncanceled p_x electron (Eq. (10.82) with $m = 1$). $\mathbf{F}_{diamagnetic}$ for the oxygen atom is

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3} + \frac{2}{3}\right)\frac{\hbar^2}{4m_e r_8^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\frac{\hbar^2}{4m_e r_8^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.156}$$

From Eqs. (10.83) and (10.89), $\mathbf{F}_{mag\,2}$ is

$$\mathbf{F}_{mag\,2} = (1+1)\frac{1}{Z}\frac{\hbar^2}{m_e r_8^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{2\hbar^2}{m_e r_8^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.157}$$

corresponding to the spin-angular-momentum contribution alone of the p_x electron and the orbital angular momentum of the p_z electron, respectively.

The outward centrifugal force on electron 8 is balanced by the electric force and the magnetic forces (on electron 8). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.155)), diamagnetic (Eq. (10.156)), and paramagnetic (Eq. (10.157)) forces as follows:

$$\frac{m_e v_8^2}{r_8} = \frac{(Z-7)e^2}{4\pi\varepsilon_o r_8^2} - \frac{\hbar^2}{4m_e r_8^2 r_3}\sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_8^2 r_3}\sqrt{s(s+1)} \tag{10.158}$$

Substitution of $v_8 = \dfrac{\hbar}{m_e r_8}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.158) gives:

$$\frac{\hbar^2}{m_e r_8^3} = \frac{(Z-7)e^2}{4\pi\varepsilon_o r_8^2} - \frac{\hbar^2}{4m_e r_8^2 r_3}\sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_8^2 r_3}\sqrt{\frac{3}{4}} \tag{10.159}$$

$$r_8 = \frac{\dfrac{\hbar^2}{m_e}}{\dfrac{(Z-7)e^2}{4\pi\varepsilon_o} - \dfrac{\hbar^2}{4m_e r_3}\sqrt{\dfrac{3}{4}} + \dfrac{2\hbar^2}{Zm_e r_3}\sqrt{\dfrac{3}{4}}} \tag{10.160}$$

$$r_8 = \frac{a_0}{(Z-7) - \left(\dfrac{1}{4} - \dfrac{2}{Z}\right)\dfrac{\sqrt{\dfrac{3}{4}}}{r_3}}, \; r_3 \text{ in units of } a_0 \tag{10.161}$$

Substitution of $\dfrac{r_3}{a_0} = 0.59020$ (Eq. (10.62) with $Z = 8$) into Eq. (10.161) gives

$$r_8 = a_0 \qquad\qquad (10.162)$$

The ionization energy of the oxygen atom is given by the negative of $E(electric)$ given by Eq. (10.102) with the appropriate charge and radius:

$$E(ionization;\ O) = -Electric\ Energy = \frac{(Z-7)e^2}{8\pi\varepsilon_o r_8} = 13.60580\ eV \qquad (10.163)$$

where $r_8 = a_0$ (Eq. (10.162)) and $Z = 8$. The experimental ionization energy of the oxygen atom is $13.6181\ eV$ [3].

THE IONIZATION ENERGIES OF EIGHT-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>8

Eight-electron atoms having $Z > 8$ possess an external electric field given by Eq. (10.92). In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that $\mathbf{F}_{diamagnetic}$ is minimized while $\mathbf{F}_{mag\,2}$ is maximized. From Eq. (10.82), the diamagnetic force, $\mathbf{F}_{diamagnetic}$, is given by the sum of the contributions from the p_x, p_y, and p_z orbitals corresponding to $m = 1$, -1, and 0, respectively:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3} + \frac{2}{3} + \frac{1}{3}\right)\frac{\hbar^2}{4m_e r_8^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{5}{3}\right)\frac{\hbar^2}{4m_e r_8^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.164)$$

The filled p orbitals with the maintenance of symmetry according to Eq. (10.72) requires that the diamagnetic force is only due to the electrons at r_3. From Eqs. (10.84) and (10.89), $\mathbf{F}_{mag\,2}$ is

$$\mathbf{F}_{mag\,2} = (4+1+1)\frac{1}{Z}\frac{\hbar^2}{m_e r_8^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{6\hbar^2}{m_e r_8^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.165)$$

corresponding to the spin and orbital angular momenta of the paired p_x electrons and the orbital angular momentum of each of the p_y and p_z electrons, respectively.

The second diamagnetic force, $\mathbf{F}_{diamagnetic\,2}$, due to the binding of the p-orbital electron having an electric field outside of its radius is given by Eq. (10.93):

$$\mathbf{F}_{diamagnetic\,2} = -\left[\frac{Z-8}{Z-7}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_8^4}10\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.166)$$

In the case that $Z > 8$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.155)), diamagnetic (Eqs. (10.164) and (10.166)), and paramagnetic (Eq. (10.165)) forces as follows:

$$\frac{m_e v_8^2}{r_8} = \frac{(Z-7)e^2}{4\pi\varepsilon_o r_8^2} - \frac{5\hbar^2}{12m_e r_8^2 r_3}\sqrt{s(s+1)} + \frac{6\hbar^2}{Zm_e r_8^2 r_3}\sqrt{s(s+1)} - \left[\frac{Z-8}{Z-7}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_8^4}10\sqrt{s(s+1)}$$

$$(10.167)$$

Substitution of $v_8 = \dfrac{\hbar}{m_e r_8}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.167) gives:

$$\frac{\hbar^2}{m_e r_8^3} = \frac{(Z-7)e^2}{4\pi\varepsilon_0 r_8^2} - \frac{5\hbar^2}{12 m_e r_8^2 r_3}\sqrt{\frac{3}{4}} + \frac{6\hbar^2}{Z m_e r_8^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-8}{Z-7}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3 \hbar^2}{r_8^4 m_e}10\sqrt{\frac{3}{4}}$$

$$(10.168)$$

The quadratic equation corresponding to Eq. (10.168) is

$$\left(\frac{(Z-7)e^2}{4\pi\varepsilon_0} - \left(\frac{5}{12} - \frac{6}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)r_8^2 - \frac{\hbar^2}{m_e}r_8 - \left[\frac{Z-8}{Z-7}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3 \hbar^2}{m_e}10\sqrt{\frac{3}{4}} = 0$$

$$(10.169)$$

$$r_8^2 - \frac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-7)e^2}{4\pi\varepsilon_0} - \left(\dfrac{5}{12} - \dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)}r_8 - \frac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-8}{Z-7}\right]\left(1 - \dfrac{\sqrt{2}}{2}\right)r_3 10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-7)e^2}{4\pi\varepsilon_0} - \left(\dfrac{5}{12} - \dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)} = 0$$

$$(10.170)$$

The solution of Eq. (10.170) using the quadratic formula is:

$$r_8 = \frac{\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-7)e^2}{4\pi\varepsilon_0} - \left(\dfrac{5}{12} - \dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)} \pm \sqrt{\left(\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-7)e^2}{4\pi\varepsilon_0} - \left(\dfrac{5}{12} - \dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)}\right)^2 + 4\dfrac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-8}{Z-7}\right]\left(1 - \dfrac{\sqrt{2}}{2}\right)r_3 10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-7)e^2}{4\pi\varepsilon_0} - \left(\dfrac{5}{12} - \dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)}}}{2}$$

$$(10.171)$$

$$r_8 = \frac{\dfrac{a_0}{\left((Z-7) - \left(\dfrac{5}{24} - \dfrac{3}{Z}\right)\dfrac{\sqrt{3}}{r_3}\right)} \pm a_0\sqrt{\left(\dfrac{1}{\left((Z-7) - \left(\dfrac{5}{24} - \dfrac{3}{Z}\right)\dfrac{\sqrt{3}}{r_3}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\dfrac{Z-8}{Z-7}\right]\left(1 - \dfrac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-7) - \left(\dfrac{5}{24} - \dfrac{3}{Z}\right)\dfrac{\sqrt{3}}{r_3}\right)}}}{2}$$

$$(10.172)$$

r_3 *in units of* a_0

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where r_3 is given by Eq. (10.62). The positive root of Eq. (10.172) must be taken in order that $r_8 > 0$. The final radius of electron 8, r_8, is given by Eq. (10.172); this is also the final radius of electrons 5, 6, and 7. The radii of several eight-electron atoms are given in Table 10.6.

The ionization energies for the eight-electron atoms with $Z > 8$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii, r_8, given by Eq. (10.172)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-7)e^2}{8\pi\varepsilon_o r_8} \qquad (10.173)$$

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured eight-electron atoms are given in Table 10.6.

Table 10.6.   Ionization energies for some eight-electron atoms.

8 e Atom	Z	r_1 (a_o)[a]	r_3 (a_o)[b]	r_8 (a_o)[c]	Theoretical Ionization Energies[d] (eV)	Experimental Ionization Energies[e] (eV)	Relative Error[f]
O	8	0.12739	0.59020	1.00000	13.60580	13.6181	0.0009
F^+	9	0.11297	0.51382	0.7649	35.5773	34.9708	-0.0173
Ne^{2+}	10	0.10149	0.45511	0.6514	62.6611	63.45	0.0124
Na^{3+}	11	0.09213	0.40853	0.5592	97.3147	98.91	0.0161
Mg^{4+}	12	0.08435	0.37065	0.4887	139.1911	141.27	0.0147
Al^{5+}	13	0.07778	0.33923	0.4338	188.1652	190.49	0.0122
Si^{6+}	14	0.07216	0.31274	0.3901	244.1735	246.5	0.0094
P^{7+}	15	0.06730	0.29010	0.3543	307.1791	309.6	0.0078
S^{8+}	16	0.06306	0.27053	0.3247	377.1579	379.55	0.0063
Cl^{9+}	17	0.05932	0.25344	0.2996	454.0940	455.63	0.0034
Ar^{10+}	18	0.05599	0.23839	0.2782	537.9756	538.96	0.0018
K^{11+}	19	0.05302	0.22503	0.2597	628.7944	629.4	0.0010
Ca^{12+}	20	0.05035	0.21308	0.2434	726.5442	726.6	0.0001
Sc^{13+}	21	0.04794	0.20235	0.2292	831.2199	830.8	-0.0005
Ti^{14+}	22	0.04574	0.19264	0.2165	942.8179	941.9	-0.0010
V^{15+}	23	0.04374	0.18383	0.2051	1061.3351	1060	-0.0013
Cr^{16+}	24	0.04191	0.17579	0.1949	1186.7691	1185	-0.0015
Mn^{17+}	25	0.04022	0.16842	0.1857	1319.1179	1317	-0.0016
Fe^{18+}	26	0.03867	0.16165	0.1773	1458.3799	1456	-0.0016
Co^{19+}	27	0.03723	0.15540	0.1696	1604.5538	1603	-0.0010
Ni^{20+}	28	0.03589	0.14961	0.1626	1757.6383	1756	-0.0009
Cu^{21+}	29	0.03465	0.14424	0.1561	1917.6326	1916	-0.0009

[a] Radius of the first set of paired inner electrons of eight-electron atoms from Eq. (10.51).
[b] Radius of the second set of paired inner electrons of eight-electron atoms from Eq. (10.62).
[c] Radius of the two paired and two unpaired outer electrons of eight-electron atoms from Eq. (10.172) for $Z > 8$ and Eq. (10.162) for O.
[d] Calculated ionization energies of eight-electron atoms given by the electric energy (Eq. (10.173)).
[e] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].
[f] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.6 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy.   In this case, the experimental capability is three to four significant figures which is consistent with the last column.   The oxygen atom isoelectronic series is given in Table 10.6 [2-3] to much higher

precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of O isoelectronic and Rydberg series, as well as direct experimental data.

NINE-ELECTRON ATOMS

Nine-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, seven, and eight-electron atoms.

RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE FLUORINE ATOM

For each eight-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), and two paired and unpaired electrons is in an orbitsphere at r_8 given by Eq. (10.172). For $Z \geq 9$, the next electron which binds to form the corresponding nine-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons. A paramagnetic spin-paring force that results in the formation of a filled s orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (7.15) with the radius r_9) reduces the energy of the atom less than that due to the alternative forces on an unpaired electron in a p_y orbital and two pairs of electrons of opposite spin in p_x and p_z orbitals of an orbitsphere at the same radius r_9. The resulting electron configuration is $1s^2 2s^2 2p^5$, and the orbital arrangement is

2p state

$$\underline{\uparrow \downarrow} \ \underline{\uparrow \downarrow} \ \underline{\uparrow} \qquad\qquad (10.174)$$

$$10-1$$

corresponding to the ground state $^2P^0_{3/2}$.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner eight electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-8)e^2}{4\pi\varepsilon_o r_9^2}\mathbf{i}_r \qquad\qquad (10.175)$$

for $r > r_8$.

The energy is minimized and the angular momentum is conserved with the pairing of electron nine to fill the p_z orbital when the orbital angular momenta of each set of p_x and p_z spin-paired electrons adds negatively to cancel. Then, the diamagnetic force (Eq. (10.82)), $\mathbf{F}_{diamagnetic}$, is

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right)\frac{\hbar^2}{4m_e r_9^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.176}$$

corresponding to $m = -1$ for the unpaired p_y electron.

From Eqs. (10.83) and (10.89), $\mathbf{F}_{mag\,2}$ is

$$\mathbf{F}_{mag\,2} = (1+1+1)\frac{1}{Z}\frac{\hbar^2}{m_e r_9^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{3\hbar^2}{m_e r_9^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.177}$$

corresponding to the spin-angular-momentum contribution alone from each of the p_x and p_z orbitals and the orbital-angular-momentum contribution of the p_z electron, respectively.

The outward centrifugal force on electron 9 is balanced by the electric force and the magnetic forces (on electron 9). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.175)), diamagnetic (Eq. (10.176)), and paramagnetic (Eq. (10.177)) forces as follows:

$$\frac{m_e v_9^2}{r_9} = \frac{(Z-8)e^2}{4\pi\varepsilon_o r_9^2} - \frac{\hbar^2}{6m_e r_9^2 r_3}\sqrt{s(s+1)} + \frac{3\hbar^2}{Zm_e r_9^2 r_3}\sqrt{s(s+1)} \tag{10.178}$$

Substitution of $v_9 = \dfrac{\hbar}{m_e r_9}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.178) gives:

$$\frac{\hbar^2}{m_e r_9^3} = \frac{(Z-8)e^2}{4\pi\varepsilon_o r_9^2} - \frac{\hbar^2}{6m_e r_9^2 r_3}\sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Zm_e r_9^2 r_3}\sqrt{\frac{3}{4}} \tag{10.179}$$

$$r_9 = \frac{\dfrac{\hbar^2}{m_e}}{\dfrac{(Z-8)e^2}{4\pi\varepsilon_o} - \dfrac{\hbar^2}{6m_e r_3}\sqrt{\dfrac{3}{4}} + \dfrac{3\hbar^2}{Zm_e r_3}\sqrt{\dfrac{3}{4}}} \tag{10.180}$$

$$r_9 = \frac{a_0}{(Z-8) - \left(\dfrac{1}{6} - \dfrac{3}{Z}\right)\dfrac{\sqrt{\dfrac{3}{4}}}{r_3}}, \; r_3 \text{ in units of } a_0 \tag{10.181}$$

Substitution of $\dfrac{r_3}{a_0} = 0.51382$ (Eq. (10.62) with $Z = 9$) into Eq. (10.181) gives

$$r_9 = 0.78069a_0 \tag{10.182}$$

The ionization energy of the fluorine atom is given by the negative of $E(electric)$ given by Eq. (10.102) with the appropriate charge and radius:

$$E(\text{ionization; } F) = -\text{Electric Energy} = \frac{(Z-8)e^2}{8\pi\varepsilon_o r_9} = 17.42782 \ eV \qquad (10.183)$$

where $r_9 = 0.78069a_0$ (Eq. (10.183)) and $Z = 9$. The experimental ionization energy of the fluorine atom is $17.42282 \ eV$ [3].

THE IONIZATION ENERGIES OF NINE-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>9

Nine-electron atoms having $Z > 9$ possess an external electric field given by Eq. (10.92). In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that $\mathbf{F}_{diamagnetic}$ is minimized while $\mathbf{F}_{mag\,2}$ is maximized. From Eq. (10.82), the diamagnetic force, $\mathbf{F}_{diamagnetic}$, is given by the sum of the contributions from the p_x, p_y, and p_z orbitals corresponding to $m = 1, -1$, and 0, respectively:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3} + \frac{2}{3} + \frac{1}{3}\right)\frac{\hbar^2}{4m_e r_9^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{5}{3}\right)\frac{\hbar^2}{4m_e r_9^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.184)$$

The filled p orbitals with the maintenance of symmetry according to Eq. (10.72) requires that the diamagnetic force is only due to the electrons at r_3. From Eqs. (10.84) and (10.89), $\mathbf{F}_{mag\,2}$ is

$$\mathbf{F}_{mag\,2} = (4 + 4 + 1)\frac{1}{Z}\frac{\hbar^2}{m_e r_9^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{9\hbar^2}{m_e r_9^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.185)$$

corresponding to the spin and orbital angular momenta of the paired p_x and p_z electrons and the orbital angular momentum of the unpaired p_y electron, respectively.

The second diamagnetic force, $\mathbf{F}_{diamagnetic\,2}$, due to the binding of the p-orbital electron having an electric field outside of its radius is given by Eq. (10.93):

$$\mathbf{F}_{diamagnetic\,2} = -\left[\frac{Z-9}{Z-8}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_9^4}10\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.186)$$

In the case that $Z > 9$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.175)), diamagnetic (Eqs. (10.184) and (10.186)), and paramagnetic (Eq. (10.185)) forces as follows:

$$\frac{m_e v_9^2}{r_9} = \frac{(Z-8)e^2}{4\pi\varepsilon_o r_9^2} - \frac{5\hbar^2}{12m_e r_9^2 r_3}\sqrt{s(s+1)} + \frac{9\hbar^2}{Zm_e r_9^2 r_3}\sqrt{s(s+1)} - \left[\frac{Z-9}{Z-8}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_9^4}10\sqrt{s(s+1)} \qquad (10.187)$$

Substitution of $v_9 = \dfrac{\hbar}{m_e r_9}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.187) gives:

$$\frac{\hbar^2}{m_e r_9^3} = \frac{(Z-8)e^2}{4\pi\varepsilon_o r_9^2} - \frac{5\hbar^2}{12m_e r_9^2 r_3}\sqrt{\frac{3}{4}} + \frac{9\hbar^2}{Zm_e r_9^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-9}{Z-8}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_9^4 m_e}10\sqrt{\frac{3}{4}}$$

$$(10.188)$$

The quadratic equation corresponding to Eq. (10.188) is

$$\left(\frac{(Z-8)e^2}{4\pi\varepsilon_o}-\left(\frac{5}{12}-\frac{9}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)r_9^2-\frac{\hbar^2}{m_e}r_9-\left[\frac{Z-9}{Z-8}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e}10\sqrt{\frac{3}{4}}=0$$

$$(10.189)$$

$$r_9^2-\frac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-8)e^2}{4\pi\varepsilon_o}-\left(\dfrac{5}{12}-\dfrac{9}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)}r_9-\frac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-9}{Z-8}\right]\left(1-\dfrac{\sqrt{2}}{2}\right)r_3 10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-8)e^2}{4\pi\varepsilon_o}-\left(\dfrac{5}{12}-\dfrac{9}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)}=0$$

$$(10.190)$$

The solution of Eq. (10.190) using the quadratic formula is:

$$r_9=\frac{\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-8)e^2}{4\pi\varepsilon_o}-\left(\dfrac{5}{12}-\dfrac{9}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)}\pm\sqrt{\left(\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-8)e^2}{4\pi\varepsilon_o}-\left(\dfrac{5}{12}-\dfrac{9}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)}\right)^2+4\dfrac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-9}{Z-8}\right]\left(1-\dfrac{\sqrt{2}}{2}\right)r_3 10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-8)e^2}{4\pi\varepsilon_o}-\left(\dfrac{5}{12}-\dfrac{9}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)}}}{2}$$

$$(10.191)$$

$$r_9=\frac{\dfrac{a_0}{\left((Z-8)-\left(\dfrac{5}{24}-\dfrac{9}{2Z}\right)\dfrac{\sqrt{3}}{r_3}\right)}\pm a_0\sqrt{\left(\dfrac{1}{\left((Z-8)-\left(\dfrac{5}{24}-\dfrac{9}{2Z}\right)\dfrac{\sqrt{3}}{r_3}\right)}\right)^2+\dfrac{20\sqrt{3}\left(\left[\dfrac{Z-9}{Z-8}\right]\left(1-\dfrac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-8)-\left(\dfrac{5}{24}-\dfrac{9}{2Z}\right)\dfrac{\sqrt{3}}{r_3}\right)}}}{2}$$

$$(10.192)$$

r_3 in units of a_0

where r_3 is given by Eq. (10.62). The positive root of Eq. (10.192) must be taken in order that $r_9 > 0$. The final radius of electron 9, r_9, is given by Eq. (10.192); this is also the final radius of electrons 5, 6, 7, and 8. The radii of several nine-electron atoms are given in Table 10.7.

The ionization energies for the nine-electron atoms with $Z > 9$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii, r_9,

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given by Eq. (10.192)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-8)e^2}{8\pi\varepsilon_o r_9}$$ (10.193)

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured nine-electron atoms are given in Table 10.7.

Table 10.7. Ionization energies for some nine-electron atoms.

9e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_9 (a_o) [c]	Theoretical Ionization Energies [d] (eV)	Experimental Ionization Energies [e] (eV)	Relative Error [f]
F	9	0.11297	0.51382	0.78069	17.42782	17.42282	-0.0003
Ne^+	10	0.10149	0.45511	0.64771	42.0121	40.96328	-0.0256
Na^{2+}	11	0.09213	0.40853	0.57282	71.2573	71.62	0.0051
Mg^{3+}	12	0.08435	0.37065	0.50274	108.2522	109.2655	0.0093
Al^{4+}	13	0.07778	0.33923	0.44595	152.5469	153.825	0.0083
Si^{5+}	14	0.07216	0.31274	0.40020	203.9865	205.27	0.0063
P^{6+}	15	0.06730	0.29010	0.36283	262.4940	263.57	0.0041
S^{7+}	16	0.06306	0.27053	0.33182	328.0238	328.75	0.0022
Cl^{8+}	17	0.05932	0.25344	0.30571	400.5466	400.06	-0.0012
Ar^{9+}	18	0.05599	0.23839	0.28343	480.0424	478.69	-0.0028
K^{10+}	19	0.05302	0.22503	0.26419	566.4968	564.7	-0.0032
Ca^{11+}	20	0.05035	0.21308	0.24742	659.8992	657.2	-0.0041
Sc^{12+}	21	0.04794	0.20235	0.23266	760.2415	756.7	-0.0047
Ti^{13+}	22	0.04574	0.19264	0.21957	867.5176	863.1	-0.0051
V^{14+}	23	0.04374	0.18383	0.20789	981.7224	976	-0.0059
Cr^{15+}	24	0.04191	0.17579	0.19739	1102.8523	1097	-0.0053
Mn^{16+}	25	0.04022	0.16842	0.18791	1230.9038	1224	-0.0056
Fe^{17+}	26	0.03867	0.16165	0.17930	1365.8746	1358	-0.0058
Co^{18+}	27	0.03723	0.15540	0.17145	1507.7624	1504.6	-0.0021
Ni^{19+}	28	0.03589	0.14961	0.16427	1656.5654	1648	-0.0052
Cu^{20+}	29	0.03465	0.14424	0.15766	1812.2821	1804	-0.0046

[a] Radius of the first set of paired inner electrons of nine-electron atoms from Equation (10.51).

[b] Radius of the second set of paired inner electrons of nine-electron atoms from Equation (10.62).

[c] Radius of the one unpaired and two sets of paired outer electrons of nine-electron atoms from Eq. (10.192) for $Z > 9$ and Eq. (10.182) for F.

[d] Calculated ionization energies of nine-electron atoms given by the electric energy (Eq. (10.193)).

[e] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

[f] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.7 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The fluorine atom isoelectronic series is given in Table 10.7 [2-3] to much higher

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precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of F isoelectronic and Rydberg series, as well as direct experimental data.

TEN-ELECTRON ATOMS
Ten-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, seven, eight, and nine-electron atoms.

RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE NEON ATOM
For each nine-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), and two sets of paired and an unpaired electron is in an orbitsphere at r_9 given by Eq. (10.192). For $Z \geq 10$, the next electron which binds to form the corresponding ten-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic force due to the spin-paired inner electrons. A paramagnetic spin-paring force that results in the formation of a filled s orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (7.15) with the radius r_{10}) reduces the energy of the atom less than that due to the alternative forces on three pairs of electrons of opposite spin in p_x, p_y, and p_z orbitals of an orbitsphere at the same radius r_{10}. The resulting electron configuration is $1s^2 2s^2 2p^6$, and the orbital arrangement is

2p state

$$\underline{\uparrow \downarrow} \quad \underline{\uparrow \downarrow} \quad \underline{\uparrow \downarrow} \qquad\qquad (10.194)$$
$$1 \qquad 0 \qquad -1$$

corresponding to the ground state $^1S_0$.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner nine electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-9)e^2}{4\pi\varepsilon_o r_{10}^2}\mathbf{i}_r \qquad\qquad (10.195)$$

for $r > r_9$.

The energy is minimized and the angular momentum is conserved with the pairing of electron ten to fill the p_y orbital when the orbital angular momenta of each set of the p_x, p_y, and p_z spin-paired electrons add negatively to cancel. Then, the diamagnetic force (Eq. (10.82)), $\mathbf{F}_{diamagnetic}$, is zero:

$$\mathbf{F}_{diamagnetic} = 0 \qquad (10.196)$$

From Eq. (10.83), $\mathbf{F}_{mag\,2}$ is

$$\mathbf{F}_{mag\,2} = (1+1+1)\frac{1}{Z}\frac{\hbar^2}{m_e r_{10}^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{3\hbar^2}{m_e r_{10}^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.197)$$

corresponding to the spin-angular-momentum contribution alone from each of the p_x, p_y, and p_z orbitals.

The outward centrifugal force on electron 10 is balanced by the electric force and the magnetic forces (on electron 10). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.195)), diamagnetic (Eq. (10.196)), and paramagnetic (Eq. (10.197)) forces as follows:

$$\frac{m_e v_{10}^2}{r_{10}} = \frac{(Z-9)e^2}{4\pi\varepsilon_o r_{10}^2} + \frac{3\hbar^2}{Zm_e r_{10}^2 r_3}\sqrt{s(s+1)} \qquad (10.198)$$

Substitution of $v_{10} = \dfrac{\hbar}{m_e r_{10}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.198) gives:

$$\frac{\hbar^2}{m_e r_{10}^3} = \frac{(Z-9)e^2}{4\pi\varepsilon_o r_{10}^2} + \frac{3\hbar^2}{Zm_e r_{10}^2 r_3}\sqrt{\frac{3}{4}} \qquad (10.199)$$

$$r_{10} = \frac{\dfrac{\hbar^2}{m_e}}{\dfrac{(Z-9)e^2}{4\pi\varepsilon_o} + \dfrac{3\hbar^2}{Zm_e r_3}\sqrt{\dfrac{3}{4}}} \qquad (10.200)$$

$$r_{10} = \frac{a_0}{(Z-9) + \dfrac{3}{Z}\dfrac{\sqrt{\dfrac{3}{4}}}{r_3}}, \quad r_3 \text{ in units of } a_0 \qquad (10.201)$$

Substitution of $\dfrac{r_3}{a_0} = 0.45511$ (Eq. (10.62) with $Z = 10$) into Eq. (10.201) gives

$$r_{10} = 0.63659a_0 \qquad (10.202)$$

The ionization energy of the neon atom is given by the negative of $E(electric)$ given by Eq. (10.102) with the appropriate charge and radius:

$$E(ionization;\ Ne) = -Electric\ Energy = \frac{(Z-9)e^2}{8\pi\varepsilon_o r_{10}} = 21.37296\ eV \qquad (10.203)$$

where $r_{10} = 0.63659a_0$ (Eq. (10.202)) and $Z = 10$. The experimental ionization energy of the neon atom is $21.56454\ eV$ [3].

THE IONIZATION ENERGIES OF TEN-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>10

Ten-electron atoms having $Z > 10$ possess an external electric field given by Eq. (10.92).   In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that $F_{diamagnetic}$ is minimized while $F_{mag\,2}$ is maximized.   From Eq. (10.82), the diamagnetic force, $F_{diamagnetic}$, is given by the sum of the contributions from the p_x, p_y, and p_z orbitals corresponding to $m = 1, -1$, and 0, respectively:

$$F_{diamagnetic} = -\left(\frac{2}{3}+\frac{2}{3}+\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_{10}^2 r_3}\sqrt{s(s+1)}\,\mathbf{i}_r = -\left(\frac{5}{3}\right)\frac{\hbar^2}{4m_e r_{10}^2 r_3}\sqrt{s(s+1)}\,\mathbf{i}_r \qquad (10.204)$$

The filled p orbitals with the maintenance of symmetry according to Eq. (10.72) requires that the diamagnetic force is only due to the electrons at r_3. From Eq. (10.84), $F_{mag\,2}$ is

$$F_{mag\,2} = (4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_e r_{10}^2 r_3}\sqrt{s(s+1)}\,\mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_{10}^2 r_3}\sqrt{s(s+1)}\,\mathbf{i}_r \qquad (10.205)$$

corresponding to the spin and orbital angular momenta of the paired p_x, p_y, and p_z electrons.

The second diamagnetic force, $F_{diamagnetic\,2}$, due to the binding of the p-orbital electron having an electric field outside of its radius is given by Eq. (10.93):

$$F_{diamagnetic\,2} = -\left[\frac{Z-10}{Z-9}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_{10}^4}10\sqrt{s(s+1)}\,\mathbf{i}_r \qquad (10.206)$$

In the case that $Z > 10$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.195)), diamagnetic (Eqs. (10.204) and (10.206)), and paramagnetic (Eq. (10.205)) forces as follows:

$$\frac{m_e v_{10}^2}{r_{10}} = \frac{(Z-9)e^2}{4\pi\varepsilon_o r_{10}^2} - \frac{5\hbar^2}{12m_e r_{10}^2 r_3}\sqrt{s(s+1)} + \frac{12\hbar^2}{Zm_e r_{10}^2 r_3}\sqrt{s(s+1)} - \left[\frac{Z-10}{Z-9}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_{10}^4}10\sqrt{s(s+1)} \qquad (10.207)$$

Substitution of $v_{10} = \dfrac{\hbar}{m_e r_{10}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.207) gives:

$$\frac{\hbar^2}{m_e r_{10}^3} = \frac{(Z-9)e^2}{4\pi\varepsilon_o r_{10}^2} - \frac{5\hbar^2}{12m_e r_{10}^2 r_3}\sqrt{\frac{3}{4}} + \frac{12\hbar^2}{Zm_e r_{10}^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-10}{Z-9}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_{10}^4 m_e}10\sqrt{\frac{3}{4}} \qquad (10.208)$$

The quadratic equation corresponding to Eq. (10.208) is

$$\left(\frac{(Z-9)e^2}{4\pi\varepsilon_o} - \left(\frac{5}{12}-\frac{12}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)r_{10}^2 - \frac{\hbar^2}{m_e}r_{10} - \left[\frac{Z-10}{Z-9}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e}10\sqrt{\frac{3}{4}} = 0 \qquad (10.209)$$

$$r_{10}^2 - \cfrac{\cfrac{\hbar^2}{m_e}}{\left(\cfrac{(Z-9)e^2}{4\pi\varepsilon_o} - \left(\cfrac{5}{12} - \cfrac{12}{Z}\right)\cfrac{\hbar^2}{m_e r_3}\sqrt{\cfrac{3}{4}}\right)} r_{10} - \cfrac{\cfrac{\hbar^2}{m_e}\left[\cfrac{Z-10}{Z-9}\right]\left(1 - \cfrac{\sqrt{2}}{2}\right)r_3 10\sqrt{\cfrac{3}{4}}}{\left(\cfrac{(Z-9)e^2}{4\pi\varepsilon_o} - \left(\cfrac{5}{12} - \cfrac{12}{Z}\right)\cfrac{\hbar^2}{m_e r_3}\sqrt{\cfrac{3}{4}}\right)} = 0$$

(10.210)

The solution of Eq. (10.210) using the quadratic formula is:

$$r_{10} = \cfrac{\cfrac{\cfrac{\hbar^2}{m_e}}{\left(\cfrac{(Z-9)e^2}{4\pi\varepsilon_o} - \left(\cfrac{5}{12} - \cfrac{12}{Z}\right)\cfrac{\hbar^2}{m_e r_3}\sqrt{\cfrac{3}{4}}\right)} \pm \sqrt{\left(\cfrac{\cfrac{\hbar^2}{m_e}}{\left(\cfrac{(Z-9)e^2}{4\pi\varepsilon_o} - \left(\cfrac{5}{12} - \cfrac{12}{Z}\right)\cfrac{\hbar^2}{m_e r_3}\sqrt{\cfrac{3}{4}}\right)}\right)^2 + 4\cfrac{\cfrac{\hbar^2}{m_e}\left[\cfrac{Z-10}{Z-9}\right]\left(1 - \cfrac{\sqrt{2}}{2}\right)r_3 10\sqrt{\cfrac{3}{4}}}{\left(\cfrac{(Z-9)e^2}{4\pi\varepsilon_o} - \left(\cfrac{5}{12} - \cfrac{12}{Z}\right)\cfrac{\hbar^2}{m_e r_3}\sqrt{\cfrac{3}{4}}\right)}}}{2}$$

(10.211)

$$r_{10} = \cfrac{\cfrac{a_0}{\left((Z-9) - \left(\cfrac{5}{24} - \cfrac{6}{Z}\right)\cfrac{\sqrt{3}}{r_3}\right)} \pm a_0\sqrt{\left(\cfrac{1}{\left((Z-9) - \left(\cfrac{5}{24} - \cfrac{6}{Z}\right)\cfrac{\sqrt{3}}{r_3}\right)}\right)^2 + \cfrac{20\sqrt{3}\left(\left[\cfrac{Z-10}{Z-9}\right]\left(1 - \cfrac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-9) - \left(\cfrac{5}{24} - \cfrac{6}{Z}\right)\cfrac{\sqrt{3}}{r_3}\right)}}}{2}$$

(10.212)

r_3 *in units of* a_0

where r_3 is given by Eq. (10.62). The positive root of Eq. (10.212) must be taken in order that $r_{10} > 0$. The final radius of electron 10, r_{10}, is given by Eq. (10.62); this is also the final radius of electrons 5, 6, 7, 8, and 9. The radii of several ten-electron atoms are given in Table 10.8.

The ionization energies for the ten-electron atoms with $Z > 10$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii, r_{10}, given by Eq. (10.212)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-9)e^2}{8\pi\varepsilon_o r_{10}}$$

(10.213)

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured ten-electron atoms are given in

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Table 10.8.

Table 10.8. Ionization energies for some ten-electron atoms.

10 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_{10} (a_o) [c]	Theoretical Ionization Energies [d] (eV)	Experimental Ionization Energies [e] (eV)	Relative Error [f]
Ne	10	0.10149	0.45511	0.63659	21.37296	21.56454	0.00888
Na^+	11	0.09213	0.40853	0.560945	48.5103	47.2864	-0.0259
Mg^{2+}	12	0.08435	0.37065	0.510568	79.9451	80.1437	0.0025
Al^{3+}	13	0.07778	0.33923	0.456203	119.2960	119.992	0.0058
Si^{4+}	14	0.07216	0.31274	0.409776	166.0150	166.767	0.0045
P^{5+}	15	0.06730	0.29010	0.371201	219.9211	220.421	0.0023
S^{6+}	16	0.06306	0.27053	0.339025	280.9252	280.948	0.0001
Cl^{7+}	17	0.05932	0.25344	0.311903	348.9750	348.28	-0.0020
Ar^{8+}	18	0.05599	0.23839	0.288778	424.0365	422.45	-0.0038
K^{9+}	19	0.05302	0.22503	0.268844	506.0861	503.8	-0.0045
Ca^{10+}	20	0.05035	0.21308	0.251491	595.1070	591.9	-0.0054
Sc^{11+}	21	0.04794	0.20235	0.236251	691.0866	687.36	-0.0054
Ti^{12+}	22	0.04574	0.19264	0.222761	794.0151	787.84	-0.0078
V^{13+}	23	0.04374	0.18383	0.210736	903.8853	896	-0.0088
Cr^{14+}	24	0.04191	0.17579	0.19995	1020.6910	1010.6	-0.0100
Mn^{15+}	25	0.04022	0.16842	0.19022	1144.4276	1134.7	-0.0086
Fe^{16+}	26	0.03867	0.16165	0.181398	1275.0911	1266	-0.0072
Co^{17+}	27	0.03723	0.15540	0.173362	1412.6783	1397.2	-0.0111
Ni^{18+}	28	0.03589	0.14961	0.166011	1557.1867	1541	-0.0105
Cu^{19+}	29	0.03465	0.14424	0.159261	1708.6139	1697	-0.0068
Zn^{20+}	30	0.03349	0.13925	0.153041	1866.9581	1856	-0.0059

[a] Radius of the first set of paired inner electrons of ten-electron atoms from Equation (10.51).

[b] Radius of the second set of paired inner electrons of ten-electron atoms from Equation (10.62).

[c] Radius of three sets of paired outer electrons of ten-electron atoms from Eq. (10.212)) for $Z > 10$ and Eq. (10.202) for Ne.

[d] Calculated ionization energies of ten-electron atoms given by the electric energy (Eq. (10.213)).

[e] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

[f] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.8 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy. In this case, the experimental capability is three to four

significant figures which is consistent with the last column.   The neon atom isoelectronic series is given in Table 10.8 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of Ne isoelectronic and Rydberg series, as well as direct experimental data.

GENERAL EQUATION FOR THE IONIZATION ENERGIES OF FIVE THROUGH TEN-ELECTRON ATOMS

Using the forces given by Eqs. (10.70), (10.82-10.84), (10.89), (10.93), and the radii r_3 given by Eq. (10.62), the radii of the 2p electrons of all five through ten-electron atoms may be solved exactly.   The electric energy given by Eq. (10.102) gives the corresponding exact ionization energies.   A summary of the parameters of the equations that determine the exact radii and ionization energies of all five through ten-electron atoms is given in Table 10.9.

F_{ele} and $F_{diamagnetic\ 2}$ given by Eqs. (10.70) and (10.93), respectively, are of the same form for all atoms with the appropriate nuclear charges and atomic radii. $F_{diamagnetic}$ given by Eq. (10.82) and $F_{mag\ 2}$ given by Eqs. (10.83-10.84) and (10.89) are of the same form with the appropriate factors that depend on the electron configuration wherein the electron configuration must be a minimum of energy.

For each n-electron atom having a central charge of Z times that of the proton and an electron configuration $1s^2 2s^2 2p^{n-4}$, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) and (10.51):

$$r_1 = r_2 = a_o \left[\frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)} \right] \tag{10.214}$$

two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62):

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$$r_4 = r_3 = \cfrac{\cfrac{a_0\left(1-\cfrac{\sqrt{\tfrac{3}{4}}}{Z}\right)}{\left((Z-3)-\left(\tfrac{1}{4}-\tfrac{1}{Z}\right)\tfrac{\sqrt{\tfrac{3}{4}}}{r_1}\right)} \pm a_0 \sqrt{\cfrac{\left(1-\cfrac{\sqrt{\tfrac{3}{4}}}{Z}\right)^2}{\left((Z-3)-\left(\tfrac{1}{4}-\tfrac{1}{Z}\right)\tfrac{\sqrt{\tfrac{3}{4}}}{r_1}\right)^2} + 4\cfrac{\left[\tfrac{Z-3}{Z-2}\right]r_1 10\sqrt{\tfrac{3}{4}}}{\left((Z-3)-\left(\tfrac{1}{4}-\tfrac{1}{Z}\right)\tfrac{\sqrt{\tfrac{3}{4}}}{r_1}\right)}}}{2}$$

r_1 in units of a_o

(10.215)

where r_1 is given by Eq. (10.214), and $n-4$ electrons in an orbitsphere with radius r_n given by

$$r_n = \cfrac{\cfrac{a_0}{\left((Z-(n-1))-\left(\tfrac{A}{8}-\tfrac{B}{2Z}\right)\tfrac{\sqrt{3}}{r_3}\right)} \pm a_0 \sqrt{\cfrac{1}{\left((Z-(n-1))-\left(\tfrac{A}{8}-\tfrac{B}{2Z}\right)\tfrac{\sqrt{3}}{r_3}\right)^2} + \cfrac{20\sqrt{3}\left(\left[\tfrac{Z-n}{Z-(n-1)}\right]\left(1-\tfrac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-(n-1))-\left(\tfrac{A}{8}-\tfrac{B}{2Z}\right)\tfrac{\sqrt{3}}{r_3}\right)}}}{2}$$ (10.216)

r_3 in units of a_0

where r_3 is given by Eq. (10.215), the parameter A given in Table 10.9 corresponds to the diamagnetic force, $\mathbf{F}_{diamagnetic}$, (Eq. (10.82)), and the parameter B given in Table 10.9 corresponds to the paramagnetic force, $\mathbf{F}_{mag\,2}$ (Eqs. (10.83-10.84) and (10.89)). The positive root of Eq. (10.216) must be taken in order that $r_n > 0$. The radii of several n-electron atoms are given in Tables 10.3-10.8.

The ionization energy for the boron atom is given by Eq. (10.104). The ionization energies for the n-electron atoms are given by the negative of the electric energy, $E(electric)$, (Eq. (10.102) with the radii, r_n, given by Eq. (10.216)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-(n-1))e^2}{8\pi\varepsilon_o r_n}$$ (10.217)

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured n-electron atoms are given by Eqs. (10.217) and (10.216) in Tables 10.3-10.8.

Table 10.9. Summary of the parameters of five through ten-electron atoms.

Atom Type	Electron Configuration	Ground State Term [a]	Orbital Arrangement of 2p Electrons (2p state)	Diamagnetic Force Factor A [b]	Paramagnetic Force Factor B [c]
Neutral 5 e Atom B	$1s^2 2s^2 2p^1$	$^2P^0_{1/2}$	↑ __ __ (1, 0, -1)	2	0
Neutral 6 e Atom C	$1s^2 2s^2 2p^2$	$^3P_0$	↑ ↑ __ (1, 0, -1)	$\dfrac{2}{3}$	0
Neutral 7 e Atom N	$1s^2 2s^2 2p^3$	$^4S^0_{3/2}$	↑ ↑ ↑ (1, 0, -1)	$\dfrac{1}{3}$	1
Neutral 8 e Atom O	$1s^2 2s^2 2p^4$	$^3P_2$	↑↓ ↑ ↑ (1, 0, -1)	1	2
Neutral 9 e Atom F	$1s^2 2s^2 2p^5$	$^2P^0_{3/2}$	↑↓ ↑↓ ↑ (1, 0, -1)	$\dfrac{2}{3}$	3
Neutral 10 e Atom Ne	$1s^2 2s^2 2p^6$	$^1S_0$	↑↓ ↑↓ ↑↓ (1, 0, -1)	0	3
5 e Ion	$1s^2 2s^2 2p^1$	$^2P^0_{1/2}$	↑ __ __ (1, 0, -1)	$\dfrac{5}{3}$	1
6 e Ion	$1s^2 2s^2 2p^2$	$^3P_0$	↑ ↑ __ (1, 0, -1)	$\dfrac{5}{3}$	4
7 e Ion	$1s^2 2s^2 2p^3$	$^4S^0_{3/2}$	↑ ↑ ↑ (1, 0, -1)	$\dfrac{5}{3}$	6
8 e Ion	$1s^2 2s^2 2p^4$	$^3P_2$	↑↓ ↑ ↑ (1, 0, -1)	$\dfrac{5}{3}$	6
9 e Ion	$1s^2 2s^2 2p^5$	$^2P^0_{3/2}$	↑↓ ↑↓ ↑ (1, 0, -1)	$\dfrac{5}{3}$	9
10 e Ion	$1s^2 2s^2 2p^6$	$^1S_0$	↑↓ ↑↓ ↑↓ (1, 0, -1)	$\dfrac{5}{3}$	12

[a] The theoretical ground state terms match those given by NIST [8].
[b] Eq. (10.82).
[c] Eqs. (10.83-10.84) and (10.89).

ELEVEN-ELECTRON ATOMS

Eleven-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, seven, eight, nine, and ten-electron atoms.

RADIUS AND IONIZATION ENERGY OF THE OUTER ELECTRON OF THE SODIUM ATOM

For each ten-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), and three sets of paired electrons in an orbitsphere at r_{10} given by Eq. (10.212). For $Z \geq 11$, the next electron which binds to form the corresponding eleven-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic forces due to the 3 sets of spin-paired inner electrons such that it forms and unpaired orbitsphere at radius r_{11}.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner ten electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-10)e^2}{4\pi\varepsilon_o r_{11}^2}\mathbf{i}_r \tag{10.218}$$

for $r > r_{10}$.

The spherically symmetrical closed 2p shell of eleven-electron atoms produces a diamagnetic force, $\mathbf{F}_{diamagnetic}$, that is equivalent to that of a closed s shell given by Eq. (10.11) with the appropriate radii. The inner electrons remain at their initial radii, but cause a diamagnetic force according to Lenz's law that is

$$\mathbf{F}_{diamagnetic} = -\frac{\hbar^2}{4m_e r_{11}^2 r_{10}}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.219}$$

In addition to the spin-spin interaction between electron pairs, the three sets of 2p electrons are orbitally paired. The single s orbital of the sodium atom produces a magnetic field at the position of the three sets of spin-paired 2p electrons. In order for the electrons to remain spin and orbitally paired, a corresponding diamagnetic force, $\mathbf{F}_{diamagnetic\,3}$, on electron eleven from the three sets of spin-paired electrons is given by

$$\mathbf{F}_{diamagnetic\,3} = -8\left[\frac{e^2\mu_o}{2m_e r_{10}}\right]\frac{\hbar^2}{m_e r_{11}^3}\mathbf{i}_r \tag{10.220}$$

corresponding to the p_x and p_y electrons with no interaction from the

orthogonal p_z electrons (Eq. (10.84)). As demonstrated by Eqs. (7.6-7.15), the maintenance of the invariance of the electron's angular momentum of $\hbar$, mass to charge ratio, $\frac{e}{m_e}$, and corresponding magnetic moment of a Bohr magneton, μ_B, requires that the term in brackets is be replaced by $\frac{1}{Z}$ corresponding to the relativistic correction given by Eq. (7.14). Thus, $\mathbf{F}_{diamagnetic\,3}$ is given by

$$\mathbf{F}_{diamagnetic\,3} = -\frac{1}{Z}\frac{8\hbar^2}{m_e r_{11}^3}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.221)$$

where the vector projection of the spin interaction of $\sqrt{s(s+1)} = \sqrt{\frac{3}{4}}$ is given by Eq. (7.15).

The outward centrifugal force on electron 11 is balanced by the electric force and the magnetic forces (on electron 11). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.218)) and diamagnetic (Eqs. (10.219) and (10.221)) forces as follows:

$$\frac{m_e v_{11}^2}{r_{11}} = \frac{(Z-10)e^2}{4\pi\varepsilon_o r_{11}^2} - \frac{\hbar^2}{4m_e r_{11}^2 r_{10}}\sqrt{s(s+1)} - \frac{8\hbar^2}{Zm_e r_{11}^3}\sqrt{s(s+1)} \qquad (10.222)$$

Substitution of $v_{11} = \dfrac{\hbar}{m_e r_{11}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.222) gives:

$$\frac{\hbar^2}{m_e r_{11}^3} = \frac{(Z-10)e^2}{4\pi\varepsilon_o r_{11}^2} - \frac{\hbar^2}{4m_e r_{11}^2 r_{10}}\sqrt{\frac{3}{4}} - \frac{8\hbar^2}{Zm_e r_{11}^3}\sqrt{\frac{3}{4}} \qquad (10.223)$$

$$r_{11} = \frac{\dfrac{\hbar^2}{m_e}\left(1 + \dfrac{8}{Z}\sqrt{\dfrac{3}{4}}\right)}{\dfrac{(Z-10)e^2}{4\pi\varepsilon_o} - \dfrac{\hbar^2}{4m_e r_{10}}\sqrt{\dfrac{3}{4}}} \qquad (10.224)$$

$$r_{11} = \frac{a_0\left(1 + \dfrac{8}{Z}\sqrt{\dfrac{3}{4}}\right)}{(Z-10) - \dfrac{\sqrt{\dfrac{3}{4}}}{4r_{10}}}, \ r_{10} \text{ in units of } a_0 \qquad (10.225)$$

Substitution of $\dfrac{r_{10}}{a_0} = 0.56094$ (Eq. (10.212) with $Z = 11$) into Eq. (10.225) gives

$$r_{11} = 2.65432a_0 \qquad (10.226)$$

The ionization energy of the sodium atom is given by the negative of $E(electric)$ given by Eq. (10.102) with the appropriate charge and radius:

$$E(ionization;\ Na) = -Electric\ Energy = \frac{(Z-10)e^2}{8\pi\varepsilon_o r_{11}} = 5.12592\ eV \qquad (10.227)$$

where $r_{11} = 2.65432a_0$ (Eq. (10.226)) and $Z = 11$. The experimental ionization energy of the sodium atom is $5.13908\ eV$ [3].

THE IONIZATION ENERGIES OF ELEVEN-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>11

Eleven-electron atoms having $Z > 11$ possess an external electric field given by Eq. (10.92). Since there is a source of dissipative, $\mathbf{J} \bullet \mathbf{E}$ of Eq. (10.27), the magnetic moments of the inner electrons may change due to the outer electron such that the energy of the eleven-electron atom is lowered. The orbital angular momenta of the paired p_x and p_y electrons give rise to the paramagnetic force given by Eq. (10.89) which is also equivalent to that given by Eq. (10.55):

$$\mathbf{F}_{mag\,2} = \frac{1}{Z}\frac{4\hbar^2}{m_e r_{11}^2 r_{10}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.228)$$

The diamagnetic force, $\mathbf{F}_{diamagnetic\,2}$, due to a relativistic effect with an electric field for $r > r_n$ (Eq. (10.35)) may be determined by considering the corresponding force due to the binding of a 2p electron. It was shown in the Five-Electron Atom section, that $\mathbf{F}_{diamagnetic\,2}$ for five through ten-electron atoms, is dependent on the amplitude of the orbital energy. Using the orbital energy with $\ell = 1$ (Eq. (10.90)), the energy $m_e\Delta v^2$ of Eq. (10.29) is reduced by the factor of $\left(1 - \frac{\sqrt{2}}{2}\right)$ due to the contribution of the charge-density wave of the inner electrons at r_3. Thus, $\mathbf{F}_{diamagnetic\,2}$ is given by Eq. (10.93). Conversely, the binding of a 3s electron increases the energy $m_e\Delta v^2$ of Eq. (10.29) by the factor of $\left(1 + \frac{\sqrt{2}}{2}\right)$ such that $\mathbf{F}_{diamagnetic\,2}$ becomes

$$\mathbf{F}_{diamagnetic\,2} = -\left[\frac{Z-11}{Z-10}\right]\left(1 + \frac{\sqrt{2}}{2}\right)\frac{r_{10}\hbar^2}{m_e r_{11}^4}10\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.229)$$

In the case that $Z > 11$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.218)), diamagnetic (Eq. (10.229)), and paramagnetic (Eq.(10.228)) forces as follows:

$$\frac{m_e v_{11}^2}{r_{11}} = \frac{(Z-10)e^2}{4\pi\varepsilon_o r_{11}^2} - \frac{\hbar^2}{4m_e r_{11}^2 r_{10}}\sqrt{s(s+1)} + \frac{4\hbar^2}{Zm_e r_{11}^2 r_{10}}\sqrt{s(s+1)}$$

$$- \frac{8\hbar^2}{Zm_e r_{11}^3}\sqrt{s(s+1)} - \left[\frac{Z-11}{Z-10}\right]\left(1 + \frac{\sqrt{2}}{2}\right)\frac{r_{10}\hbar^2}{m_e r_{11}^4}10\sqrt{s(s+1)} \qquad (10.230)$$

Substitution of $v_{11} = \dfrac{\hbar}{m_e r_{11}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.230) gives:

$$\frac{\hbar^2}{m_e r_{11}^3} = \frac{(Z-10)e^2}{4\pi\varepsilon_o r_{11}^2} - \frac{\hbar^2}{4 m_e r_{11}^2 r_{10}}\sqrt{\frac{3}{4}} + \frac{4\hbar^2}{Z m_e r_{11}^2 r_{10}}\sqrt{\frac{3}{4}} - \frac{8\hbar^2}{Z m_e r_{11}^3}\sqrt{\frac{3}{4}} - \left[\frac{Z-11}{Z-10}\right]\left(1+\frac{\sqrt{2}}{2}\right)\frac{r_{10}\hbar^2}{m_e r_{11}^4}10\sqrt{\frac{3}{4}}$$

(10.231)

The quadratic equation corresponding to Eq. (10.231) is

$$\left(\frac{(Z-10)e^2}{4\pi\varepsilon_o} - \left(\frac{1}{4}-\frac{4}{Z}\right)\frac{\hbar^2}{m_e r_{10}}\sqrt{\frac{3}{4}}\right)r_{11}^2 - \frac{\hbar^2}{m_e}\left(1+\frac{8\sqrt{\frac{3}{4}}}{Z}\right)r_{11} - \left[\frac{Z-11}{Z-10}\right]\left(1+\frac{\sqrt{2}}{2}\right)\frac{r_{10}\hbar^2}{m_e}10\sqrt{\frac{3}{4}} = 0$$

(10.232)

$$r_{11}^2 - \frac{\dfrac{\hbar^2}{m_e}\left(1+\dfrac{8\sqrt{\frac{3}{4}}}{Z}\right)}{\left(\dfrac{(Z-10)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{4}-\dfrac{4}{Z}\right)\dfrac{\hbar^2}{m_e r_{10}}\sqrt{\frac{3}{4}}\right)}r_{11} - \frac{\left[\dfrac{Z-11}{Z-10}\right]\left(1+\dfrac{\sqrt{2}}{2}\right)\dfrac{r_{10}\hbar^2}{m_e}10\sqrt{\frac{3}{4}}}{\left(\dfrac{(Z-10)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{4}-\dfrac{4}{Z}\right)\dfrac{\hbar^2}{m_e r_{10}}\sqrt{\frac{3}{4}}\right)} = 0$$

(10.233)

The solution of Eq. (10.233) using the quadratic formula is:

$$r_{11} = \frac{\dfrac{\dfrac{\hbar^2}{m_e}\left(1+\dfrac{8\sqrt{\frac{3}{4}}}{Z}\right)}{\left(\dfrac{(Z-10)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{4}-\dfrac{4}{Z}\right)\dfrac{\hbar^2}{m_e r_{10}}\sqrt{\frac{3}{4}}\right)} \pm \sqrt{\left(\dfrac{\dfrac{\hbar^2}{m_e}\left(1+\dfrac{8\sqrt{\frac{3}{4}}}{Z}\right)}{\left(\dfrac{(Z-10)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{4}-\dfrac{4}{Z}\right)\dfrac{\hbar^2}{m_e r_{10}}\sqrt{\frac{3}{4}}\right)}\right)^2 + 4\dfrac{\left[\dfrac{Z-11}{Z-10}\right]\left(1+\dfrac{\sqrt{2}}{2}\right)\dfrac{r_{10}\hbar^2}{m_e}10\sqrt{\frac{3}{4}}}{\left(\dfrac{(Z-10)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{4}-\dfrac{4}{Z}\right)\dfrac{\hbar^2}{m_e r_{10}}\sqrt{\frac{3}{4}}\right)}}}{2}$$

(10.234)

$$r_{11} = \cfrac{\cfrac{a_0\left(1+\cfrac{4\sqrt{3}}{Z}\right)}{\left((Z-10)-\left(\cfrac{1}{8}-\cfrac{2}{Z}\right)\cfrac{\sqrt{3}}{r_{10}}\right)} \pm a_0 \sqrt{\left(\cfrac{1+\cfrac{4\sqrt{3}}{Z}}{\left((Z-10)-\left(\cfrac{1}{8}-\cfrac{2}{Z}\right)\cfrac{\sqrt{3}}{r_{10}}\right)}\right)^2 + \cfrac{20\sqrt{3}\left(\left[\cfrac{Z-11}{Z-10}\right]\left(1+\cfrac{\sqrt{2}}{2}\right)r_{10}\right)}{\left((Z-10)-\left(\cfrac{1}{8}-\cfrac{2}{Z}\right)\cfrac{\sqrt{3}}{r_{10}}\right)}}}{2} \tag{10.235}$$

$$r_{10} \text{ in units of } a_0$$

where r_{10} is given by Eq. (10.212). The positive root of Eq. (10.235) must be taken in order that $r_{11} > 0$.   The radii of several eleven-electron atoms are given in Table 10.10.

The ionization energies for the eleven-electron atoms with $Z > 11$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii, r_{11}, given by Eq. (10.235)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-10)e^2}{8\pi\varepsilon_o r_{11}} \tag{10.236}$$

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured eleven-electron atoms are given in Table 10.10.

Table 10.10. Ionization energies for some eleven-electron atoms.

11 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_{10} (a_o) [c]	r_{11} (a_o) [d]	Theoretical Ionization Energies [e] (eV)	Experimenta l Ionization Energies [f] (eV)	Relative Error [g]
Na	11	0.09213	0.40853	0.560945	2.65432	5.12592	5.13908	0.0026
Mg^+	12	0.08435	0.37065	0.510568	1.74604	15.5848	15.03528	-0.0365
Al^{2+}	13	0.07778	0.33923	0.456203	1.47399	27.6918	28.44765	0.0266
Si^{3+}	14	0.07216	0.31274	0.409776	1.25508	43.3624	45.14181	0.0394
P^{4+}	15	0.06730	0.29010	0.371201	1.08969	62.4299	65.0251	0.0399
S^{5+}	16	0.06306	0.27053	0.339025	0.96226	84.8362	88.0530	0.0365
Cl^{6+}	17	0.05932	0.25344	0.311903	0.86151	110.5514	114.1958	0.0319
Ar^{7+}	18	0.05599	0.23839	0.288778	0.77994	139.5577	143.460	0.0272
K^{8+}	19	0.05302	0.22503	0.268844	0.71258	171.8433	175.8174	0.0226
Ca^{9+}	20	0.05035	0.21308	0.251491	0.65602	207.3998	211.275	0.0183
Sc^{10+}	21	0.04794	0.20235	0.236251	0.60784	246.2213	249.798	0.0143
Ti^{11+}	22	0.04574	0.19264	0.222761	0.56631	288.3032	291.500	0.0110
V^{12+}	23	0.04374	0.18383	0.210736	0.53014	333.6420	336.277	0.0078
Cr^{13+}	24	0.04191	0.17579	0.19995	0.49834	382.2350	384.168	0.0050
Mn^{14+}	25	0.04022	0.16842	0.19022	0.47016	434.0801	435.163	0.0025
Fe^{15+}	26	0.03867	0.16165	0.181398	0.44502	489.1753	489.256	0.0002
Co^{16+}	27	0.03723	0.15540	0.173362	0.42245	547.5194	546.58	-0.0017
Ni^{17+}	28	0.03589	0.14961	0.166011	0.40207	609.1111	607.06	-0.0034
Cu^{18+}	29	0.03465	0.14424	0.159261	0.38358	673.9495	670.588	-0.0050
Zn^{19+}	30	0.03349	0.13925	0.153041	0.36672	742.0336	738	-0.0055

[a] Radius of the first set of paired inner electrons of eleven-electron atoms from Eq. (10.51).

[b] Radius of the second set of paired inner electrons of eleven-electron atoms from Eq. (10.62).

[c] Radius of three sets of paired inner electrons of eleven-electron atoms from Eq. (10.212)).

[d] Radius of unpaired outer electron of eleven-electron atoms from Eq. (10.235)) for $Z > 11$ and Eq. (10.226) for Na.

[e] Calculated ionization energies of eleven-electron atoms given by the electric energy (Eq. (10.236)).

[f] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

[g] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.10 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The sodium atom isoelectronic series is given in Table 10.10 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these

values are based on theoretical and interpolation techniques rather than data alone.   Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of Na isoelectronic and Rydberg series, as well as direct experimental data.

TWELVE-ELECTRON ATOMS

Twelve-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, seven, eight, nine, ten, and eleven-electron atoms.

RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE MAGNESIUM ATOM

For each eleven-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), three sets of paired electrons in an orbitsphere at r_{10} given by Eq. (10.212), and an unpaired electron in an orbitsphere at r_{11}. For $Z \geq 12$, the next electron which binds to form the corresponding twelve-electron atom is attracted by the central Coulomb field and the spin-pairing force with the unpaired 3s inner electron and is repelled by diamagnetic forces due to the 3 sets of spin-paired inner electrons such that it forms and unpaired orbitsphere at radius r_{12}.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner eleven electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-11)e^2}{4\pi\varepsilon_o r_{12}^2}\mathbf{i}_r \tag{10.237}$$

for $r > r_{11}$.

The outer electron which binds to form the corresponding twelve-electron atom becomes spin-paired with the unpaired inner electron such that they become indistinguishable with the same radius $r_{11} = r_{12}$ corresponding to a filled 3s shell.   The corresponding spin-pairing force $\mathbf{F}_{mag}$ is given by Eq. (7.15):

$$\mathbf{F}_{mag} = \frac{1}{Z}\frac{\hbar^2}{m_e r_{12}^3}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.238}$$

The spherically symmetrical closed 2p shell of twelve-electron

atoms produces a diamagnetic force, $\mathbf{F}_{diamagnetic}$, that is equivalent to that of a closed s shell given by Eq. (10.11) with the appropriate radii. The inner electrons remain at their initial radii, but cause a diamagnetic force according to Lenz's law that is

$$\mathbf{F}_{diamagnetic} = -\frac{\hbar^2}{4m_e r_{12}^2 r_{10}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.239)$$

In addition to the paramagnetic spin-pairing force between the eleventh electron initially at radius r_{11}, the pairing causes the diamagnetic interaction between the outer electrons and the inner electrons given by Eq. (10.11) to vanish, except for an electrodynamic effect for $Z > 12$ described in the Two-Electron Atoms section, since upon pairing the magnetic field of the outer electrons becomes zero. Using Eq. (10.55), $\mathbf{F}_{mag\,2}$ due to the three 2p orbitals is given by:

$$\mathbf{F}_{mag\,2} = \frac{3}{Z}\frac{\hbar^2}{m_e r_{10} r_{12}^2}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.240)$$

In addition to the spin-spin interactions between electron pairs, the three sets of 2p electrons are orbitally paired. The s electrons of the magnesium atom produce a magnetic field at the position of the three sets of spin-paired 2p electrons. In order for the electrons to remain spin and orbitally paired, the corresponding diamagnetic force, $\mathbf{F}_{diamagnetic\,3}$ (Eq. (10.221)), on electron twelve from the three sets of spin-paired electrons is given by

$$\mathbf{F}_{diamagnetic\,3} = -\frac{1}{Z}\frac{12\hbar^2}{m_e r_{12}^3}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.241)$$

corresponding to the p_x, p_y, and p_z electrons.

The outward centrifugal force on electron 12 is balanced by the electric force and the magnetic forces (on electron 12). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.237)), diamagnetic (Eqs. (10.239) and (10.241)) and paramagnetic (Eqs. (10.238) and (10.240)) forces as follows:

$$\frac{m_e v_{12}^2}{r_{12}} = \frac{(Z-11)e^2}{4\pi\varepsilon_o r_{12}^2} - \frac{\hbar^2}{4m_e r_{12}^2 r_{10}}\sqrt{s(s+1)} + \frac{3\hbar^2}{Zm_e r_{12}^2 r_{10}}\sqrt{s(s+1)}$$
$$-\frac{12\hbar^2}{Zm_e r_{12}^3}\sqrt{s(s+1)} + \frac{\hbar^2}{Zm_e r_{12}^3}\sqrt{s(s+1)} \qquad (10.242)$$

Substitution of $v_{12} = \dfrac{\hbar}{m_e r_{12}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.242) gives:

$$\frac{\hbar^2}{m_e r_{12}^3} = \frac{(Z-11)e^2}{4\pi\varepsilon_o r_{12}^2} - \frac{\hbar^2}{4m_e r_{12}^2 r_{10}}\sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Zm_e r_{12}^2 r_{10}}\sqrt{\frac{3}{4}} - \frac{12\hbar^2}{Zm_e r_{12}^3}\sqrt{\frac{3}{4}} + \frac{\hbar^2}{Zm_e r_{12}^3}\sqrt{\frac{3}{4}} \qquad (10.243)$$

$$r_{12} = \frac{\dfrac{\hbar^2}{m_e}\left(1 + \dfrac{11\sqrt{\frac{3}{4}}}{Z}\right)}{\dfrac{(Z-11)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{4} - \dfrac{3}{Z}\right)\dfrac{\hbar^2}{m_e r_{10}}\sqrt{\dfrac{3}{4}}} \qquad (10.244)$$

$$r_{12} = \frac{a_0\left(1 + \dfrac{11\sqrt{\frac{3}{4}}}{Z}\right)}{(Z-11) - \left(\dfrac{1}{4} - \dfrac{3}{Z}\right)\dfrac{\sqrt{\frac{3}{4}}}{r_{10}}}, \; r_{10} \; in \; units \; of \; a_0 \qquad (10.245)$$

Substitution of $\dfrac{r_{10}}{a_0} = 0.51057$ (Eq. (10.212) with $Z = 12$) into Eq. (10.245) gives

$$r_{12} = 1.79386 a_0 \qquad (10.246)$$

The ionization energy of the magnesium atom is given by the electric energy, $E(electric)$, (Eq. (10.102) with the radius, r_{12}, given by Eq. (10.246)):

$$E(ionization; \; Mg) = -Electric \; Energy = \frac{(Z-11)e^2}{8\pi\varepsilon_o r_{12}} = 7.58467 \; eV \qquad (10.247)$$

where $r_{12} = 1.79386 a_0$ (Eq. (10.246)) and $Z = 12$. The experimental ionization energy of the magnesium atom is $7.64624 \; eV$ [3].

THE IONIZATION ENERGIES OF TWELVE-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>12

Twelve-electron atoms having $Z > 12$ possess an external electric field given by Eq. (10.92). Since there is a source of dissipative, $\mathbf{J} \bullet \mathbf{E}$ of Eq. (10.27), the magnetic moments of the inner electrons may change due to the outer electron such that the energy of the twelve-electron atom is lowered with conservation of angular momentum. Of the possible forces based on Maxwell's equations, those which give rise to an energy minimum are used to calculated the atomic radii and energies. With this constraint, the only paramagnetic force is that given by Eq. (10.89) due to the spin angular momenta of the paired $2p_x$, p_y, and p_z electrons interacting with equivalently with each of the $3s$ electrons. This force which is also equivalent to that given by Eq. (10.145) is:

$$\mathbf{F}_{mag2} = 2\frac{1}{Z}\frac{3\hbar^2}{m_e r_{12}^2 r_{10}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.248)$$

From Eq. (10.229), the diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, due to a relativistic effect with an electric field for $r > r_{12}$ (Eq. (10.35)) is

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-12}{Z-11}\right]\left(1+\frac{\sqrt{2}}{2}\right)\frac{r_{10}\hbar^2}{m_e r_{12}^4}10\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.249)$$

In the case that $Z > 12$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.237)), diamagnetic (Eq. (10.249)), and paramagnetic (Eq. (10.248)) forces as follows:

$$\frac{m_e v_{12}^2}{r_{12}} = \frac{(Z-11)e^2}{4\pi\varepsilon_o r_{12}^2} - \frac{\hbar^2}{4m_e r_{12}^2 r_{10}}\sqrt{s(s+1)} + \frac{6\hbar^2}{2m_e r_{12}^2 r_{10}}\sqrt{s(s+1)} - \left[\frac{Z-12}{Z-11}\right]\left(1+\frac{\sqrt{2}}{2}\right)\frac{r_{10}\hbar^2}{m_e r_{12}^4}10\sqrt{s(s+1)} \qquad (10.250)$$

Substitution of $v_{12} = \dfrac{\hbar}{m_e r_{12}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.250) gives:

$$\frac{\hbar^2}{m_e r_{12}^3} = \frac{(Z-11)e^2}{4\pi\varepsilon_o r_{12}^2} - \frac{\hbar^2}{4m_e r_{12}^2 r_{10}}\sqrt{\frac{3}{4}} + \frac{6\hbar^2}{2m_e r_{12}^2 r_{10}}\sqrt{\frac{3}{4}} - \left[\frac{Z-12}{Z-11}\right]\left(1+\frac{\sqrt{2}}{2}\right)\frac{r_{10}\hbar^2}{m_e r_{12}^4}10\sqrt{\frac{3}{4}} \qquad (10.251)$$

The quadratic equation corresponding to Eq. (10.251) is

$$\left(\frac{(Z-11)e^2}{4\pi\varepsilon_o} - \left(\frac{1}{4}-\frac{6}{Z}\right)\frac{\hbar^2}{m_e r_{10}}\sqrt{\frac{3}{4}}\right)r_{12}^2 - \frac{\hbar^2}{m_e}r_{12} - \left[\frac{Z-12}{Z-11}\right]\left(1+\frac{\sqrt{2}}{2}\right)\frac{r_{10}\hbar^2}{m_e}10\sqrt{\frac{3}{4}} = 0 \qquad (10.252)$$

$$r_{12}^2 - \frac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-11)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{4}-\dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_{10}}\sqrt{\dfrac{3}{4}}\right)}r_{12} - \frac{\left[\dfrac{Z-12}{Z-11}\right]\left(1+\dfrac{\sqrt{2}}{2}\right)\dfrac{r_{10}\hbar^2}{m_e}10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-11)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{4}-\dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_{10}}\sqrt{\dfrac{3}{4}}\right)} = 0 \qquad (10.253)$$

The solution of Eq. (10.253) using the quadratic formula is:

$$r_{12} = \frac{\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-11)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{4}-\dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_{10}}\sqrt{\dfrac{3}{4}}\right)} \pm \sqrt{\left(\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-11)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{4}-\dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_{10}}\sqrt{\dfrac{3}{4}}\right)}\right)^2 + 4\dfrac{\left[\dfrac{Z-12}{Z-11}\right]\left(1+\dfrac{\sqrt{2}}{2}\right)\dfrac{r_{10}\hbar^2}{m_e}10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-11)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{4}-\dfrac{6}{Z}\right)\dfrac{\hbar^2}{m_e r_{10}}\sqrt{\dfrac{3}{4}}\right)}}}{2}$$

$$\qquad (10.254)$$

$$r_{12} = \cfrac{\cfrac{a_0}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)} \pm a_0 \sqrt{\left(\cfrac{1}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}\right)^2 + \cfrac{20\sqrt{3}\left(\left[\frac{Z-12}{Z-11}\right]\left(1+\frac{\sqrt{2}}{2}\right)r_{10}\right)}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}}}{2} \qquad (10.255)$$

$$r_{10} \text{ in units of } a_0$$

where r_{10} is given by Eq. (10.212). The positive root of Eq. (10.255) must be taken in order that $r_{12} > 0$.   The radii of several twelve-electron atoms are given in Table 10.11.

The ionization energies for the twelve-electron atoms with $Z > 12$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii, r_{12}, given by Eq. (10.255)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-11)e^2}{8\pi\varepsilon_o r_{12}} \qquad (10.256)$$

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured twelve-electron atoms are given in Table 10.11.

Table 10.11. Ionization energies for some twelve-electron atoms.

12 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_{10} (a_o) [c]	r_{12} (a_o) [d]	Theoretical Ionization Energies [e] (eV)	Experimental Ionization Energies [f] (eV)	Relative Error [g]
Mg	12	0.08435	0.37065	0.51057	1.79386	7.58467	7.64624	0.0081
Al^+	13	0.07778	0.33923	0.45620	1.41133	19.2808	18.82856	-0.0240
Si^{2+}	14	0.07216	0.31274	0.40978	1.25155	32.6134	33.49302	0.0263
P^{3+}	15	0.06730	0.29010	0.37120	1.09443	49.7274	51.4439	0.0334
S^{4+}	16	0.06306	0.27053	0.33902	0.96729	70.3296	72.5945	0.0312
Cl^{5+}	17	0.05932	0.25344	0.31190	0.86545	94.3266	97.03	0.0279
Ar^{6+}	18	0.05599	0.23839	0.28878	0.78276	121.6724	124.323	0.0213
K^{7+}	19	0.05302	0.22503	0.26884	0.71450	152.3396	154.88	0.0164
Ca^{8+}	20	0.05035	0.21308	0.25149	0.65725	186.3102	188.54	0.0118
Sc^{9+}	21	0.04794	0.20235	0.23625	0.60857	223.5713	225.18	0.0071
Ti^{10+}	22	0.04574	0.19264	0.22276	0.56666	264.1138	265.07	0.0036
V^{11+}	23	0.04374	0.18383	0.21074	0.53022	307.9304	308.1	0.0006
Cr^{12+}	24	0.04191	0.17579	0.19995	0.49822	355.0157	354.8	-0.0006
Mn^{13+}	25	0.04022	0.16842	0.19022	0.46990	405.3653	403.0	-0.0059
Fe^{14+}	26	0.03867	0.16165	0.18140	0.44466	458.9758	457	-0.0043
Co^{15+}	27	0.03723	0.15540	0.17336	0.42201	515.8442	511.96	-0.0076
Ni^{16+}	28	0.03589	0.14961	0.16601	0.40158	575.9683	571.08	-0.0086
Cu^{17+}	29	0.03465	0.14424	0.15926	0.38305	639.3460	633	-0.0100
Zn^{18+}	30	0.03349	0.13925	0.15304	0.36617	705.9758	698	-0.0114

[a] Radius of the first set of paired inner electrons of twelve-electron atoms from Eq. (10.51).

[b] Radius of the second set of paired inner electrons of twelve-electron atoms from Eq. (10.62).

[c] Radius of three sets of paired inner electrons of twelve-electron atoms from Eq. (10.212)).

[d] Radius of paired outer electrons of twelve-electron atoms from Eq. (10.255)) for $Z > 12$ and Eq. (10.246) for Mg.

[e] Calculated ionization energies of twelve-electron atoms given by the electric energy (Eq. (10.256)).

[f] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

[g] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.11 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The magnesium atom isoelectronic series is given in Table 10.11 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather

than data alone.   Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of Mg isoelectronic and Rydberg series, as well as direct experimental data.

3P-ORBITAL ELECTRONS BASED ON AN ENERGY MINIMUM

For each thirteen through eighteen-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), three sets of paired electrons in an orbitsphere at r_{10} given by Eq. (10.212), and two indistinguishable spin-paired electrons in an orbitsphere with radii r_{11} and r_{12} both given by Eq. (10.255).   For $Z \geq 12$, the next electron which binds to form the corresponding n-electron atom ($13 \leq n \leq 18$) is attracted by the central Coulomb field and is repelled by diamagnetic forces and attracted by paramagnetic forces due to the 3 sets of spin-paired inner 2p electrons and two spin-paired inner 3s electrons such that it forms an orbitsphere comprising all of the 3p electrons at radius r_n.   The resulting electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^{n-12}$.

The central Coulomb force, $\mathbf{F}_{ele}$, acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner $n-1$ electrons is given by Eq. (10.70):

$$\mathbf{F}_{ele} = \frac{(Z - (n-1))e^2}{4\pi\varepsilon_o r_n^2}\mathbf{i}_r \qquad (10.257)$$

for $r > r_{n-1}$ where n corresponds to the number of electrons of the atom and Z is its atomic number.   In each case, the magnetic field of the binding outer electron changes the angular velocities of the inner electrons.   However, in each case, the magnetic field of the outer electron provides a central Lorentzian force which exactly balances the change in centrifugal force because of the change in angular velocity [1].   The inner electrons remain at their initial radii, but cause a diamagnetic force according to Lenz's law.

As shown in the 2P-Orbital Electrons Based on an Energy Minimum section the quantum numbers $\ell = 1$ $m = \pm 1$ and $\ell = 1$ $m = 0$ correspond to spherical harmonics solutions, $Y_\ell^m(\theta,\phi)$, of Laplace's equation designated the $2p_x$, $2p_y$, and $2p_z$ orbitals, respectively.   Similarly, for $13 \leq n \leq 18$, the energy may be lowered by filling 3p orbitals in the same manner to achieve an energy minimum relative to other configurations and arrangements.   In general, a nonuniform distribution of charge achieves

an energy minimum with the formation of a fifth shell due to the dependence of the magnetic forces on the nuclear charge and orbital energy (Eqs. (10.70), (10.258-10.264), and (10.268)). The outer electrons of atoms and ions that are isoelectronic with the series aluminum through argon half-fill a 3p level with unpaired electrons at phosphorous, then fill the level with paired electrons at argon.

Similarly to the case of the 2p orbitals, spherical harmonic charge-density waves may be induced in the inner electron orbitspheres with the addition of one or more outer electrons to the 3p orbitals. An energy minimum is achieved when the thirteenth through eighteenth electrons of each thirteen through eighteen-electron atom fills a 3p orbital with the formation of orthogonal complementary charge-density waves in the inner shell 2p and 3s electrons. To maintain the symmetry of the central charge and the energy minimum condition given by solutions to Laplace's equation (Eq. (10.72)), the charge-density waves on electron orbitspheres at r_{10} and r_{12} complement those of the outer orbitals when the outer 3p orbitals are not all occupied by at least one electron, and the complementary charge-density waves are provided by electrons at r_{12} when this condition is met. In the case of the 3p electrons, an exception to the trends in 2p orbital forces arises due to the interaction between the 2p, 3s, and 3p electrons due to magnetic fields independent of induced complementary charge-density waves. The spin and angular momenta of the 2p electrons give rise to corresponding magnetic fields that interact with the two 3s electrons. The filled 2p orbitals with the maintenance of symmetry according to Laplace's equation (Eq. (10.72)) requires that the 2p as well as the 3s electrons contribute forces to the 3p electrons due to the electrons at r_{10} acing on the electrons at r_{12} which complies with the reactive force, $\mathbf{F}_{diamagnetic\,2}$, having the factor $\left(1 + \frac{\sqrt{2}}{2}\right)$ and given by Eq. (10.229).

The total orbital contribution to the diamagnetic force, $\mathbf{F}_{diamagnetic}$, given by Eq. (10.82) is:

$$\mathbf{F}_{diamagnetic} = -\sum_m \frac{(\ell + |m|)!}{(2\ell + 1)(\ell - |m|)!} \frac{\hbar^2}{4m_e r_n^2 r_{12}} \sqrt{s(s+1)}\mathbf{i}_r \qquad (10.258)$$

where the contributions from orbitals having $|m| = 1$ add positively or negatively. From Eq. (10.204), the diamagnetic force, $\mathbf{F}_{diamagnetic}$, contribution from the 2p electrons is given by the sum of the contributions from the p_x, p_y, and p_z orbitals corresponding to $m = 1, -1,$ and 0, respectively:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3} + \frac{2}{3} + \frac{1}{3}\right) \frac{\hbar^2}{4m_e r_n^2 r_{12}} \sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{5}{3}\right) \frac{\hbar^2}{4m_e r_n^2 r_{12}} \sqrt{s(s+1)}\mathbf{i}_r \qquad (10.259)$$

where r_{12} is given by Eq. (10.255). Due to the 2p-3s-3p interaction, the 3s electrons provide spin or orbital angular momentum in order conserve angular momentum of the interacting orbitals. In the case that an energy minimum is achieved with 3s orbital angular momentum, the diamagnetic force, $\mathbf{F}_{diamagnetic}$, contribution is given by Eqs. (10.82) and (10.258) where $m = 1, -1$, or 0 corresponding to induced charge-density waves. The contribution from the 3s orbital is added to the contributions from the 3p and the 2p orbitals until the 3p orbitals are at least half filled. Then the diamagnetic force is only due to 3p and 3s electrons since the induced charge-density waves only involve the inner-most shell, the 3s orbital.

As given by Eq. (10.89), the contribution of the orbital angular momentum of an unpaired 3p electron to the paramagnetic force, $\mathbf{F}_{mag\,2}$, is

$$\mathbf{F}_{mag\,2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)}\mathbf{i}_r \qquad (10.260)$$

Each outer 3p electron contributes spin as well as orbital angular momentum. The former gives rise to spin pairing to another 3p electron when an energy minimum is achieved. In the case that the orbital angular momenta of paired 3p electrons cancel, the contribution to $\mathbf{F}_{mag\,2}$ due to spin alone given by Eq. (10.83) is equivalent to that due to orbital angular momentum alone (Eq. (10.260)). Due to the 2p-3s-3p interaction, the 3s electrons can also provide a paramagnetic force, $\mathbf{F}_{mag\,2}$, contribution given by Eqs. (10.82) and (10.260) due to spin angular momentum corresponding to induced charge-density waves.

N-electron atoms having $Z > n$ possess an electric field given by Eq. (10.92) for $r > r_n$. Since there is a source of dissipative, $\mathbf{J} \bullet \mathbf{E}$ of Eq. (10.27), the magnetic moments of the inner electrons may change due to the outer electron such that the energy of the n-electron atom is lowered. $\mathbf{F}_{diamagnetic}$, is given by Eqs. (10.82) and (10.258). Due to the 2p-3s-3p interaction, the 2p level contributes to the forces even when the filling of the 3p level is half or greater, and the 3s electrons may provide orbital angular momentum in order conserve angular momentum of the interacting orbitals. In the case that an energy minimum is achieved with 3s orbital angular momentum, the diamagnetic force, $\mathbf{F}_{diamagnetic}$, contribution is given by Eqs. (10.82) and (10.258) where $m = 1, -1$, or 0 corresponding to induced charge-density waves. The contribution from the 3s orbital is added to the contributions from the 3p and the 2p orbitals.

Due to the 2p-3s-3p interaction with $Z > n$, $\mathbf{F}_{mag\,2}$ has a contribution from the 2p, 3s, and 3p orbitals. The filled 2p orbitals with the maintenance of symmetry according to Eq. (10.72) requires that the

diamagnetic force, $\mathbf{F}_{mag\,2}$, contribution is

$$\mathbf{F}_{mag\,2} = (4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.261)$$

corresponding to the spin and orbital angular momenta of the paired $2p_x$, p_y, and p_z electrons (Eq. (10.205)). The 3s electrons can provide a $\mathbf{F}_{mag\,2}$ contribution of

$$\mathbf{F}_{mag\,2} = \frac{1}{Z}\frac{4\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.262)$$

corresponding to coupling to the spin and induced orbital angular momentum wherein the orbitals interact such that this contribution superimposes negatively or positively to the contributions from the 2p and 3p orbitals. Each outer 3p electron contributes spin as well as orbital angular momentum. Each unpaired 3p electron can spin and orbitally pair with a 2p orbital. The corresponding force, $\mathbf{F}_{mag\,2}$, contribution given by Eq. (10.84) is:

$$\mathbf{F}_{mag\,2} = \frac{1}{Z}\frac{4\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.263)$$

The 3p electrons spin-pair upon further filling of the 3p orbital. Two spin-paired 3p electrons interacting with two spin-paired 2p orbital electrons double the corresponding force, $\mathbf{F}_{mag\,2}$, contribution:

$$\mathbf{F}_{mag\,2} = \frac{1}{Z}\frac{8\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.264)$$

The sum of the magnitude of the angular momentum of the electron is $\hbar$ in any inertial frame and is relativistically invariant. The vector projections of the orbitsphere spin angular momentum relative to the Cartesian coordinates are given in the Spin Angular Momentum of the Orbitsphere with $\boldsymbol{\mathit{l}} = 0$ section. The magnitude of the z-axis projection of the spin angular momentum, $|L_z|$, the moment of inertia about the z-axis, I_z, and the rotational energy about the z-axis, $E_{rotational\,spin}$, given by Eqs. (1.78-1.82) are

$$|L_z| = I\frac{\hbar}{m_e r^2} = \frac{\hbar}{2} \qquad (10.265)$$

$$I_z = I_{spin} = \frac{m_e r_n^2}{2} \qquad (10.266)$$

$$E_{rotational} = E_{rotational\,spin} = \frac{1}{4}\left[\frac{\hbar^2}{2I_{spin}}\right] = \frac{1}{4}\left[\frac{\hbar^2}{m_e r_n^2}\right] \qquad (10.267)$$

N-electron atoms having $Z > n$ possess an electric field given by Eq. (10.92) for $r > r_n$. Since there is a source of dissipative, $\mathbf{J} \bullet \mathbf{E}$ of Eq. (10.27), the magnetic moments of the inner electrons may change due to the

outer electron such that the energy of the n-electron atom is lowered.   As shown in the P-Orbital Electrons Based on an Energy Minimum section for $F_{diamagnetic\,2}$ given by Eq. (10.93), the corresponding diamagnetic force for 2p electrons, $F_{diamagnetic\,2}$, due to a relativistic effect with an electric field for $r > r_n$ (Eq. (10.35)) is dependent on the amplitude of the orbital energy. Using the orbital energy with $\ell = 1$ (Eq. (10.90)), the energy $m_e \Delta v^2$ of Eq. (10.29) is reduced by the factor of $\left(1 - \dfrac{\sqrt{2}}{2}\right)$ due to the contribution of the charge-density wave of the inner electrons at r_{12}.   In addition, the two 3s electrons contribute an energy factor based on Eq. (1.82) since the filled 2p orbitals with the maintenance of symmetry according to Eq. (10.72) requires that the diamagnetic force is due to the electrons at r_{10} acing on the electrons at r_{12} which complies with the reactive force, $F_{diamagnetic\,2}$, given by Eq. (10.229).   Thus, $F_{diamagnetic\,2}$ for 3p electrons with $Z > n$ is given by

$$F_{diamagnetic\,2} = -\left[\frac{Z-n}{Z-(n-1)}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_n^4}10\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.268)$$

The total diamagnetic and paramagnetic forces are given as the sum over the orbital and spin angular momenta that may add positively or negatively while maintaining the conservation of angular momentum.   Of the possible forces based on Maxwell's equations, those which give rise to an energy minimum are used to calculated the atomic radii and energies. In general, an energy minimum is achieved by minimizing $F_{diamagnetic}$ while maximizing $F_{mag\,2}$ with conservation of angular momentum.

Using the forces given by Eqs. (10.257-10.264), (10.268), and the radii r_{12} given by Eq. (10.255), the radii of the 3p electrons of all thirteen through eighteen-electron atoms may be solved exactly.   The electric energy given by Eq. (10.102) gives the corresponding exact ionization energies. F_{ele} and $F_{diamagnetic\,2}$ given by Eqs. (10.257) and (10.268), respectively, are of the same form for all atoms with the appropriate nuclear charges and atomic radii. $F_{diamagnetic}$ given by Eq. (10.258) and $F_{mag\,2}$ given by Eqs. (10.260-10.264) are of the same form with the appropriate factors that depend on the minimum-energy electron configuration.   The general equation and the summary of the parameters that determine the exact radii and ionization energies of all thirteen through eighteen-electron atoms are given the General Equation For The Ionization Energies of Thirteen Through Eighteen-Electron Atoms section and in Table 10.18.

THIRTEEN-ELECTRON ATOMS

Thirteen-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, seven, eight, nine, ten,

eleven, and twelve-electron atoms.

RADIUS AND IONIZATION ENERGY OF THE OUTER ELECTRON OF THE ALUMINUM ATOM

For each twelve-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), three sets of paired electrons in an orbitsphere at r_{10} given by Eq. (10.212), and two indistinguishable spin-paired electrons in an orbitsphere with radii r_{11} and r_{12} both given by Eq. (10.255). For $Z \geq 13$, the next electron which binds to form the corresponding thirteen-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic forces due to the 3 sets of spin-paired inner 2p electrons and two spin-paired inner 3s electrons such that it forms and unpaired orbitsphere at radius r_{13}. The resulting electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^1$, and the orbital arrangement is

3p state

$$\underline{\uparrow} \quad \underline{} \quad \underline{} \qquad \qquad (10.269)$$
$$ 1 \quad\; 0 \quad -1$$

corresponding to the ground state $^2P_{1/2}^0$.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner twelve electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-12)e^2}{4\pi\varepsilon_o r_{13}^2} \mathbf{i}_r \qquad\qquad (10.270)$$

for $r > r_{12}$.

As in the case of the boron atom given in the Five-Electron Atom section, the single p orbital of the aluminum atom produces a diamagnetic force equivalent to that of the formation of an s orbital due to the induction of complementary and spherically symmetrical charge-density waves on electron orbitspheres at r_{10} and r_{12} in order to achieve a solution of Laplace's equation (Eq. (10.72)). The inner electrons remain at their initial radii, but cause a diamagnetic force according to Lenz's law that is given by Eq. (10.96) with the appropriate radii. In addition, the contribution of the diamagnetic force, $\mathbf{F}_{diamagnetic}$, due to the 2p electrons is given by Eqs. (10.105) and (10.259) as the sum of the contributions from the p_x, p_y, and p_z orbitals corresponding to $m = 1$, -1, and 0, respectively.

Thus, $\mathbf{F}_{diamagnetic}$ is given by

$$\mathbf{F}_{diamagnetic} = -\left(2 + \frac{2}{3} + \frac{2}{3} + \frac{1}{3}\right)\frac{\hbar^2}{4m_e r_{13}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{11}{3}\right)\frac{\hbar^2}{4m_e r_{13}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.271)$$

The charge induction forms complementary mirror charge-density waves which must have opposing angular momenta such that momentum is conserved. In this case, $\mathbf{F}_{mag\,2}$ given by Eq. (10.260) is zero:

$$\mathbf{F}_{mag\,2} = 0 \qquad (10.272)$$

The outward centrifugal force on electron 13 is balanced by the electric force and the magnetic force (on electron 13). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.270)) and diamagnetic (Eq. (10.271)) forces as follows:

$$\frac{m_e v_{13}^2}{r_{13}} = \frac{(Z-12)e^2}{4\pi\varepsilon_o r_{13}^2} - \frac{\frac{11}{3}\hbar^2}{4m_e r_{13}^2 r_{12}}\sqrt{s(s+1)} \qquad (10.273)$$

Substitution of $v_{13} = \dfrac{\hbar}{m_e r_{13}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.273) gives:

$$\frac{\hbar^2}{m_e r_{13}^3} = \frac{(Z-12)e^2}{4\pi\varepsilon_o r_{13}^2} - \frac{11\hbar^2}{12m_e r_{13}^2 r_{12}}\sqrt{\frac{3}{4}} \qquad (10.274)$$

$$r_{13} = \frac{a_0}{\left((Z-12) - \dfrac{11\sqrt{\dfrac{3}{4}}}{12r_{12}}\right)}, \; r_{12} \text{ in units of } a_0 \qquad (10.275)$$

Substitution of $\dfrac{r_{12}}{a_0} = 1.41133$ (Eq. (10.255) with $Z = 13$) into Eq. (10.275)

gives

$$r_{13} = 2.28565a_0 \qquad (10.276)$$

The energy stored in the electric field of the aluminum atom, $E(electric)$, is given by Eq. (10.102) with the appropriate with the radius, r_{13}, given by Eq. (10.276)):

$$E(electric); \; Al) = -\frac{(Z-12)e^2}{8\pi\varepsilon_o r_{13}} = 5.95270 \; eV \qquad (10.277)$$

where $r_{13} = 2.28565a_0$ (Eq. (10.276)) and $Z = 13$. The ionization energy is given by the sum of the electric energy and the energy corresponding to the change in magnetic-moments of the inner shell electrons. Since there is no source of dissipative power, $\mathbf{J} \bullet \mathbf{E}$ of Eq. (10.27), to compensate for any potential change in the magnetic moments, Δm, of the inner electrons due to the ionization of the outer electron of the aluminum atom, there is a diamagnetic energy term in the ionization energy for this atom that

follows from the corresponding term for the lithium atom given by Eqs. (10.15-10.24), with $Z = 13$, r_{12} given by Eq. (10.255), and r_{13} given by Eq. (10.276). Thus, the change in magnetic energy of the inner orbitsphere at r_{12} is 76.94147 %, so that the corresponding energy ΔE_{mag} is

$$\Delta E_{mag} = 0.7694147 \times 0.04069938 \ eV = 0.0313147 \ eV \tag{10.278}$$

where the magnetic energy of the inner electrons is $0.04069938 \ eV$ (Eqs. (10.64) and (10.276)). Then, the ionization energy of the aluminum atom is given by Eqs. (10.276-10.278):

$$E(ionization; \ Al) = \frac{(Z-12)e^2}{8\pi\varepsilon_o r_{13}} + \Delta E_{mag} \tag{10.279}$$

$$= 5.95270 \ eV + 0.031315 \ eV = 5.98402 \ eV$$

The experimental ionization energy of the boron atom is $5.98577 \ eV$ [3].

THE IONIZATION ENERGIES OF THIRTEEN-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>13

Thirteen-electron atoms having $Z > 13$ possess an external electric field given by Eq. (10.92). In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that $\mathbf{F}_{diamagnetic}$ is minimized while $\mathbf{F}_{mag \ 2}$ is maximized. From Eq. (10.258), the diamagnetic force, $\mathbf{F}_{diamagnetic}$, is given by the sum of the contributions from the $2p_x$, p_y, and p_z orbitals corresponding to $m = 1, -1$, and 0, respectively:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3} + \frac{2}{3} + \frac{1}{3}\right)\frac{\hbar^2}{4m_e r_{13}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{5}{3}\right)\frac{\hbar^2}{4m_e r_{13}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.280}$$

wherein the contribution due to the $3p_x$ ($m = 1$) is canceled by the mirror charge-density wave with $m = -1$ induced in the 3s orbital according to Eq. (10.258).

With $Z > 13$, the charge induction forms complementary mirror charge-density waves such that the angular momenta do not cancel. The filled 2p orbitals with the maintenance of symmetry according to Eq. (10.72) requires that the diamagnetic force is due to the electrons at r_{10} acing on the electrons at r_{12} which complies with the reactive force, $\mathbf{F}_{diamagnetic \ 2}$, given by Eq. (10.249). From Eq. (10.261), $\mathbf{F}_{mag \ 2}$ is

$$\mathbf{F}_{mag \ 2} = (4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_e r_{13}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_{13}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.281}$$

corresponding to the spin and orbital angular momenta of the paired $2p_x$, p_y, and p_z electrons wherein the contribution due to the $3p_x$ ($m = 1$) is canceled by the mirror charge-density wave with $m = -1$ induced in the 3s orbital according to Eq. (10.262).

The diamagnetic force, $\mathbf{F}_{diamagnetic \ 2}$, due to the binding of the 3p-orbital

electron having an electric field outside of its radius is given by Eq. (10.268):

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-13}{Z-12}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{13}^4}10\sqrt{s(s+1)}\mathbf{i}_r$$ (10.282)

In the case that $Z > 13$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.270)) and diamagnetic (Eqs. (10.280) and (10.282)), and paramagnetic (Eq. (10.281)) forces as follows:

$$\frac{m_e v_{13}^2}{r_{13}} = \frac{(Z-12)e^2}{4\pi\varepsilon_o r_{13}^2} - \frac{5\hbar^2}{12m_e r_{13}^2 r_{12}}\sqrt{s(s+1)} + \frac{12\hbar^2}{Zm_e r_{13}^2 r_{12}}\sqrt{s(s+1)}$$

$$-\left[\frac{Z-13}{Z-12}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{r_{13}^4 m_e}10\sqrt{s(s+1)}$$ (10.283)

Substitution of $v_{13} = \dfrac{\hbar}{m_e r_{13}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.283) gives:

$$\frac{\hbar^2}{m_e r_{13}^3} = \frac{(Z-12)e^2}{4\pi\varepsilon_o r_{13}^2} - \frac{5\hbar^2}{12m_e r_{13}^2 r_{12}}\sqrt{\frac{3}{4}} + \frac{12\hbar^2}{Zm_e r_{13}^2 r_{12}}\sqrt{\frac{3}{4}} - \left[\frac{Z-13}{Z-12}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{r_{13}^4 m_e}10\sqrt{\frac{3}{4}}$$ (10.284)

The quadratic equation corresponding to Eq. (10.284) is

$$\left(\frac{(Z-12)e^2}{4\pi\varepsilon_o} - \left(\frac{5}{12} - \frac{12}{Z}\right)\frac{\hbar^2}{m_e r_{12}}\sqrt{\frac{3}{4}}\right)r_{13}^2 - \frac{\hbar^2}{m_e}r_{13} - \left[\frac{Z-13}{Z-12}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e}10\sqrt{\frac{3}{4}} = 0$$ (10.285)

$$r_{13}^2 - \frac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-12)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{12}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}r_{13} - \frac{\left[\dfrac{Z-13}{Z-12}\right]\left(1 - \dfrac{\sqrt{2}}{2} + \dfrac{1}{2}\right)\dfrac{r_{12}\hbar^2}{m_e}10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-12)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{12}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)} = 0$$ (10.286)

The solution of Eq. (10.286) using the quadratic formula is:

$$r_{13} = \frac{\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-12)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{12}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)} \pm \sqrt{\left(\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-12)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{12}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}\right)^2 + 4\dfrac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-13}{Z-12}\right]\left(1 - \dfrac{\sqrt{2}}{2} + \dfrac{1}{2}\right)r_{12}10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-12)e^2}{4\pi\varepsilon_o} - \left(\dfrac{5}{12} - \dfrac{12}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}}}{2}$$ (10.287)

$$r_{13} = \cfrac{\cfrac{a_0}{\left((Z-12)-\left(\dfrac{5}{24}-\dfrac{6}{Z}\right)\dfrac{\sqrt{3}}{r_{12}}\right)} \pm a_0 \sqrt{\left(\cfrac{1}{\left((Z-12)-\left(\dfrac{5}{24}-\dfrac{6}{Z}\right)\dfrac{\sqrt{3}}{r_{12}}\right)}\right)^2 + \cfrac{20\sqrt{3}\left(\left[\dfrac{Z-13}{Z-12}\right]\left(1-\dfrac{\sqrt{2}}{2}+\dfrac{1}{2}\right)r_{12}\right)}{\left((Z-12)-\left(\dfrac{5}{24}-\dfrac{6}{Z}\right)\dfrac{\sqrt{3}}{r_{12}}\right)}}}{2} \tag{10.288}$$

r_{12} *in units of* a_0

where r_{12} is given by Eq. (10.255). The positive root of Eq. (10.288) must be taken in order that $r_{13} > 0$. The radii of several thirteen-electron atoms are given in Table 10.12.

The ionization energies for the thirteen-electron atoms with $Z > 13$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii, r_{13}, given by Eq. (10.288)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-12)e^2}{8\pi\varepsilon_o r_{13}} \tag{10.289}$$

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured thirteen-electron atoms are given in Table 10.12.

Table 10.12. Ionization energies for some thirteen-electron atoms.

13 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_{10} (a_o) [c]	r_{12} (a_o) [d]	r_{13} (a_o) [e]	Theoretical Ionization Energies [f] (eV)	Experimental Ionization Energies [g] (eV)	Relative Error [h]
Al	13	0.07778	0.33923	0.45620	1.41133	2.28565	5.98402	5.98577	0.0003
Si^+	14	0.07216	0.31274	0.40978	1.25155	1.5995	17.0127	16.34585	-0.0408
P^{2+}	15	0.06730	0.29010	0.37120	1.09443	1.3922	29.3195	30.2027	0.0292
S^{3+}	16	0.06306	0.27053	0.33902	0.96729	1.1991	45.3861	47.222	0.0389
Cl^{4+}	17	0.05932	0.25344	0.31190	0.86545	1.0473	64.9574	67.8	0.0419
Ar^{5+}	18	0.05599	0.23839	0.28878	0.78276	0.9282	87.9522	91.009	0.0336
K^{6+}	19	0.05302	0.22503	0.26884	0.71450	0.8330	114.3301	117.56	0.0275
Ca^{7+}	20	0.05035	0.21308	0.25149	0.65725	0.7555	144.0664	147.24	0.0216
Sc^{8+}	21	0.04794	0.20235	0.23625	0.60857	0.6913	177.1443	180.03	0.0160
Ti^{9+}	22	0.04574	0.19264	0.22276	0.56666	0.6371	213.5521	215.92	0.0110
V^{10+}	23	0.04374	0.18383	0.21074	0.53022	0.5909	253.2806	255.7	0.0095
Cr^{11+}	24	0.04191	0.17579	0.19995	0.49822	0.5510	296.3231	298.0	0.0056
Mn^{12+}	25	0.04022	0.16842	0.19022	0.46990	0.5162	342.6741	343.6	0.0027
Fe^{13+}	26	0.03867	0.16165	0.18140	0.44466	0.4855	392.3293	392.2	-0.0003
Co^{14+}	27	0.03723	0.15540	0.17336	0.42201	0.4583	445.2849	444	-0.0029
Ni^{15+}	28	0.03589	0.14961	0.16601	0.40158	0.4341	501.5382	499	-0.0051
Cu^{16+}	29	0.03465	0.14424	0.15926	0.38305	0.4122	561.0867	557	-0.0073
Zn^{17+}	30	0.03349	0.13925	0.15304	0.36617	0.3925	623.9282	619	-0.0080

[a] Radius of the paired 1s inner electrons of thirteen-electron atoms from Eq. (10.51).

[b] Radius of the paired 2s inner electrons of thirteen-electron atoms from Eq. (10.62).

[c] Radius of the three sets of paired 2p inner electrons of thirteen-electron atoms from Eq. (10.212)).

[d] Radius of the paired 3s inner electrons of thirteen-electron atoms from Eq. (10.255)).

[e] Radius of the unpaired 3p outer electron of thirteen-electron atoms from Eq. (10.288) for $Z > 13$ and Eq. (10.276) for Al.

[f] Calculated ionization energies of thirteen-electron atoms given by the electric energy (Eq. (10.289)) for $Z > 13$ and Eq. (10.279) for Al.

[g] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

[h] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.12 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The aluminum atom isoelectronic series is given in Table 10.12 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than

data alone. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of Al isoelectronic and Rydberg series, as well as direct experimental data.

FOURTEEN-ELECTRON ATOMS

Fourteen-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, seven, eight, nine, ten, eleven, twelve, and thirteen-electron atoms.

RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE SILICON ATOM

For each thirteen-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), three sets of paired electrons in an orbitsphere at r_{10} given by Eq. (10.212), two indistinguishable spin-paired electrons in an orbitsphere with radii r_{11} and r_{12} both given by Eq. (10.255), and an unpaired electron in an orbitsphere with radius r_{13} given by Eq. (10.288). For $Z \geq 14$, the next electron which binds to form the corresponding fourteen-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic forces due to the 3 sets of spin-paired inner 2p electrons and two spin-paired inner 3s electrons. A paramagnetic spin-paring force to form a filled s orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (7.15) with the radius r_{14}) reduces the energy of the atom less than that due to the alternative forces on two unpaired 3p electrons in an orbitsphere at the same radius r_{14}. The resulting electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^2$, and the orbital arrangement is

3p state

$$\underline{\uparrow} \quad \underline{\uparrow} \quad \underline{} \qquad\qquad\qquad (10.290)$$

$$1 \qquad 0 \qquad -1$$

corresponding to the ground state $^3P_0$.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner thirteen electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-13)e^2}{4\pi\varepsilon_o r_{14}^2}\mathbf{i}_r \qquad\qquad\qquad (10.291)$$

for $r > r_{13}$.

As in the case of the carbon atom given in the Six-Electron Atom section, the two orthogonal 3p electrons form charge-density waves such that the total angular momentum of the two outer electrons is conserved which determines the diamagnetic force according to Eq. (10.82) (Eq. (10.258)).   The contribution is given by Eq. (10.117) corresponding to $m = 1$.   In addition, the contribution of the diamagnetic force, $\mathbf{F}_{diamagnetic}$, due to the 2p electrons is given by Eq. (10.105) (Eq. (10.259)) as the sum of the contributions from the 2 p_x, p_y, and p_z orbitals corresponding to $m = 1, -1$, and 0, respectively.   Thus, $\mathbf{F}_{diamagnetic}$ is given by

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3} + \frac{2}{3} + \frac{2}{3} + \frac{1}{3}\right)\frac{\hbar^2}{4m_e r_{14}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$= -\left(\frac{7}{3}\right)\frac{\hbar^2}{4m_e r_{14}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.292)$$

The charge induction forms complementary mirror charge-density waves which must have opposing angular momenta such that momentum is conserved.   In this case, $\mathbf{F}_{mag\,2}$ given by Eq. (10.89) (Eq. (10.260)) is zero:

$$\mathbf{F}_{mag\,2} = 0 \qquad (10.293)$$

The outward centrifugal force on electron 14 is balanced by the electric force and the magnetic forces (on electron 14).   The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.291)) and diamagnetic (Eq. (10.292)) forces as follows:

$$\frac{m_e v_{14}^2}{r_{14}} = \frac{(Z-13)e^2}{4\pi\varepsilon_o r_{14}^2} - \frac{7\hbar^2}{12 m_e r_{14}^2 r_{12}}\sqrt{s(s+1)} \qquad (10.294)$$

Substitution of $v_{14} = \dfrac{\hbar}{m_e r_{14}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.294) gives:

$$\frac{\hbar^2}{m_e r_{14}^3} = \frac{(Z-13)e^2}{4\pi\varepsilon_o r_{14}^2} - \frac{7\hbar^2}{12 m_e r_{14}^2 r_{12}}\sqrt{s(s+1)} \qquad (10.295)$$

$$r_{14} = \frac{a_0}{\left((Z-13) - \dfrac{7\sqrt{\dfrac{3}{4}}}{12 r_{12}}\right)}, \; r_{12} \text{ in units of } a_0 \qquad (10.296)$$

Substitution of $\dfrac{r_{12}}{a_0} = 1.25155$ (Eq. (10.255) with $Z = 14$) into Eq. (10.296) gives

$$r_{14} = 1.67685 a_0 \qquad (10.297)$$

The ionization energy of the silicon atom is given by the electric energy, $E(electric)$, (Eq. (10.102) with the radius, r_{14}, given by Eq. (10.297)):

$$E(\text{ionization}; \ Si) = -\text{Electric Energy} = \frac{(Z - 13)e^2}{8\pi\varepsilon_o r_{14}} = 8.11391 \ eV \qquad (10.298)$$

where $r_{14} = 1.67685a_0$ (Eq. (10.297)) and $Z = 14$.   The experimental ionization energy of the silicon atom is $8.15169 \ eV$ [3].

THE IONIZATION ENERGIES OF FOURTEEN-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>14

Fourteen-electron atoms having $Z > 14$ possess an external electric field given by Eq. (10.92).   In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that $\mathbf{F}_{diamagnetic}$ is minimized while $\mathbf{F}_{mag\ 2}$ is maximized.   With a half-filled 3p shell, the diamagnetic force due to the orbital angular momenta of the 3p electrons cancels that of the 2p electrons.   Thus, $\mathbf{F}_{diamagnetic}$ is minimized by the formation of a charge-density wave in the 3s orbital corresponding to $m = -1$ in Eq. (10.258) to form the equivalent of a half-filled 3p shell such that the contribution due to the 2p shell is canceled. From Eq. (10.258), the diamagnetic force, $\mathbf{F}_{diamagnetic}$, is given by the sum of the contributions from the $3p_x$ and p_z orbitals corresponding to $m = 1$ and 0, respectively, and the negative contribution due to the charge-density wave with $m = -1$ induced in the 3s orbital according to Eq. (10.258):

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3} + \frac{1}{3} - \frac{2}{3}\right)\frac{\hbar^2}{4m_e r_{14}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_{14}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.299)$$

From Eq. (10.261), $\mathbf{F}_{mag\ 2}$ corresponding to the spin and orbital angular momenta of the paired $2p_x$, p_y, and p_z electrons is

$$\mathbf{F}_{mag\ 2} = (4 + 4 + 4)\frac{1}{Z}\frac{\hbar^2}{m_e r_{14}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_{14}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.300)$$

and the contribution from the 3p shell is

$$\mathbf{F}_{mag\ 2} = (4 + 4 - 4)\frac{1}{Z}\frac{\hbar^2}{m_e r_{14}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{4\hbar^2}{m_e r_{14}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.301)$$

corresponding to the $3p_x$ and p_z electrons wherein the contribution due to the $3p_x$ ($m = 1$) electron is canceled by the mirror charge-density wave with $m = -1$ induced in the 3s orbital (Eq. (10.262)).   Thus, the total of $\mathbf{F}_{mag\ 2}$ is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{16\hbar^2}{m_e r_{14}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.302)$$

The diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, due to the binding of the 3p-orbital electron having an electric field outside of its radius is given by Eq. (10.268):

$$\mathbf{F}_{diamagnetic\,2} = -\left[\frac{Z-14}{Z-13}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{14}^4}10\sqrt{s(s+1)}\,\mathbf{i}_r \qquad (10.303)$$

In the case that $Z>14$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.291)), diamagnetic (Eqs. (10.299) and (10.303)), and paramagnetic (Eq. (10.302)) forces as follows:

$$\frac{m_e v_{14}^2}{r_{14}} = \frac{(Z-13)e^2}{4\pi\varepsilon_o r_{14}^2} - \frac{\hbar^2}{12m_e r_{14}^2 r_{12}}\sqrt{s(s+1)} + \frac{16\hbar^2}{Zm_e r_{14}^2 r_{12}}\sqrt{s(s+1)}$$

$$-\left[\frac{Z-14}{Z-13}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{14}^4}10\sqrt{s(s+1)} \qquad (10.304)$$

Substitution of $v_{14} = \dfrac{\hbar}{m_e r_{14}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.304) gives:

$$\frac{\hbar^2}{m_e r_{14}^3} = \frac{(Z-13)e^2}{4\pi\varepsilon_o r_{14}^2} - \frac{\hbar^2}{12m_e r_{14}^2 r_{12}}\sqrt{\frac{3}{4}} + \frac{16\hbar^2}{Zm_e r_{14}^2 r_{12}}\sqrt{\frac{3}{4}} - \left[\frac{Z-14}{Z-13}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{14}^4}10\sqrt{\frac{3}{4}} \qquad (10.305)$$

The quadratic equation corresponding to Eq. (10.305) is

$$\left(\frac{(Z-13)e^2}{4\pi\varepsilon_o} - \left(\frac{1}{12}-\frac{16}{Z}\right)\frac{\hbar^2}{m_e r_{12}}\sqrt{\frac{3}{4}}\right)r_{14}^2 - \frac{\hbar^2}{m_e}r_{14} - \left[\frac{Z-14}{Z-13}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e}10\sqrt{\frac{3}{4}} = 0 \qquad (10.306)$$

$$r_{14}^2 - \frac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-13)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{12}-\dfrac{16}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}r_{14} - \frac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-14}{Z-13}\right]\left(1-\dfrac{\sqrt{2}}{2}+\dfrac{1}{2}\right)r_{12}10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-13)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{12}-\dfrac{16}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)} = 0 \qquad (10.307)$$

The solution of Eq. (10.307) using the quadratic formula is:

$$r_{14} = \frac{\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-13)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{12}-\dfrac{16}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)} \pm \sqrt{\left(\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-13)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{12}-\dfrac{16}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}\right)^2 + 4\dfrac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-14}{Z-13}\right]\left(1-\dfrac{\sqrt{2}}{2}+\dfrac{1}{2}\right)r_{12}10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-13)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{12}-\dfrac{16}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}}}{2}$$

$$(10.308)$$

$$r_{14} = \cfrac{\cfrac{a_0}{\left((Z-13)-\left(\dfrac{1}{24}-\dfrac{8}{Z}\right)\dfrac{\sqrt{3}}{r_{12}}\right)} \pm a_0 \sqrt{\left(\cfrac{1}{\left((Z-13)-\left(\dfrac{1}{24}-\dfrac{8}{Z}\right)\dfrac{\sqrt{3}}{r_{12}}\right)}\right)^2 + \cfrac{20\sqrt{3}\left(\left[\dfrac{Z-14}{Z-13}\right]\left(1-\dfrac{\sqrt{2}}{2}+\dfrac{1}{2}\right)r_{12}\right)}{\left((Z-13)-\left(\dfrac{1}{24}-\dfrac{8}{Z}\right)\dfrac{\sqrt{3}}{r_{12}}\right)}}}{2}$$

(10.309)

$$r_{12} \text{ in units of } a_0$$

where r_{12} is given by Eq. (10.255). The positive root of Eq. (10.309) must be taken in order that $r_{14} > 0$. The final radius of electron 14, r_{14}, is given by Eq. (10.309); this is also the final radius of electron 13.   The radii of several fourteen-electron atoms are given in Table 10.13.

The ionization energies for the fourteen-electron atoms with $Z > 14$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii r_{14}, given by Eq. (10.309)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-13)e^2}{8\pi\varepsilon_o r_{14}}$$

(10.310)

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured fourteen-electron atoms are given in Table 10.13.

Table 10.13. Ionization energies for some fourteen-electron atoms.

14 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_{10} (a_o) [c]	r_{12} (a_o) [d]	r_{14} (a_o) [e]	Theoretical Ionization Energies [f] (eV)	Experimental Ionization Energies [g] (eV)	Relative Error [h]
Si	14	0.07216	0.31274	0.40978	1.25155	1.67685	8.11391	8.15169	0.0046
P^+	15	0.06730	0.29010	0.37120	1.09443	1.35682	20.0555	19.7694	-0.0145
S^{2+}	16	0.06306	0.27053	0.33902	0.96729	1.21534	33.5852	34.790	0.0346
Cl^{3+}	17	0.05932	0.25344	0.31190	0.86545	1.06623	51.0426	53.4652	0.0453
Ar^{4+}	18	0.05599	0.23839	0.28878	0.78276	0.94341	72.1094	75.020	0.0388
K^{5+}	19	0.05302	0.22503	0.26884	0.71450	0.84432	96.6876	99.4	0.0273
Ca^{6+}	20	0.05035	0.21308	0.25149	0.65725	0.76358	124.7293	127.2	0.0194
Sc^{7+}	21	0.04794	0.20235	0.23625	0.60857	0.69682	156.2056	158.1	0.0120
Ti^{8+}	22	0.04574	0.19264	0.22276	0.56666	0.64078	191.0973	192.10	0.0052
V^{9+}	23	0.04374	0.18383	0.21074	0.53022	0.59313	229.3905	230.5	0.0048
Cr^{10+}	24	0.04191	0.17579	0.19995	0.49822	0.55211	271.0748	270.8	-0.0010
Mn^{11+}	25	0.04022	0.16842	0.19022	0.46990	0.51644	316.1422	314.4	-0.0055
Fe^{12+}	26	0.03867	0.16165	0.18140	0.44466	0.48514	364.5863	361	-0.0099
Co^{13+}	27	0.03723	0.15540	0.17336	0.42201	0.45745	416.4021	411	-0.0131
Ni^{14+}	28	0.03589	0.14961	0.16601	0.40158	0.43277	471.5854	464	-0.0163
Cu^{15+}	29	0.03465	0.14424	0.15926	0.38305	0.41064	530.1326	520	-0.0195
Zn^{16+}	30	0.03349	0.13925	0.15304	0.36617	0.39068	592.0410	579	-0.0225

[a] Radius of the paired 1s inner electrons of fourteen-electron atoms from Eq. (10.51).

[b] Radius of the paired 2s inner electrons of fourteen-electron atoms from Eq. (10.62).

[c] Radius of the three sets of paired 2p inner electrons of fourteen-electron atoms from Eq. (10.212)).

[d] Radius of the paired 3s inner electrons of fourteen-electron atoms from Eq. (10.255)).

[e] Radius of the two unpaired 3p outer electrons of fourteen-electron atoms from Eq. (10.309) for $Z > 14$ and Eq. (10.297) for Si.

[f] Calculated ionization energies of fourteen-electron atoms given by the electric energy (Eq. (10.310)).

[g] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

[h] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.13 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The silicon atom isoelectronic series is given in Table 10.13 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off

of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of Si isoelectronic and Rydberg series, as well as direct experimental data.

FIFTEEN-ELECTRON ATOMS

Fifteen-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, seven, eight, nine, ten, eleven, twelve, thirteen and fourteen-electron atoms.

RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE PHOSPHOROUS ATOM

For each fourteen-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), three sets of paired electrons in an orbitsphere at r_{10} given by Eq. (10.212), two indistinguishable spin-paired electrons in an orbitsphere with radii r_{11} and r_{12} both given by Eq. (10.255), and two unpaired electrons in an orbitsphere with radius r_{14} given by Eq. (10.288). For $Z \geq 15$, the next electron which binds to form the corresponding fifteen-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic forces due to the 3 sets of spin-paired inner 2p electrons and two spin-paired inner 3s electrons. A paramagnetic spin-paring force to form a filled s orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (7.15) with the radius r_{15}) reduces the energy of the atom less than that due to the alternative forces on three unpaired 3p electrons in an orbitsphere at the same radius r_{15}. The resulting electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^3$, and the orbital arrangement is

3p state

$$\underline{\uparrow} \quad \underline{\uparrow} \quad \underline{\uparrow} \qquad\qquad (10.311)$$
$$\quad 1 \qquad 0 \qquad -1$$

corresponding to the ground state $^4S^0_{3/2}$.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner fourteen electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-14)e^2}{4\pi\varepsilon_o r_{15}^2} \mathbf{i}_r \qquad\qquad (10.312)$$

for $r > r_{14}$.

The diamagnetic force, $\mathbf{F}_{diamagnetic}$, is only due to 3p and 3s electrons when the 3p shell is at least half filled since the induced charge-density waves only involve the inner-most shell, the 3s orbital. Thus, $\mathbf{F}_{diamagnetic}$, is given by Eq. (10.259) as the sum of the contributions from the $3\,p_x$, p_y, and p_z orbitals corresponding to $m = 1, -1,$ and 0, respectively:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}+\frac{2}{3}+\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_{15}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{5}{3}\right)\frac{\hbar^2}{4m_e r_{15}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.313)$$

The energy is minimized with conservation of angular momentum when the spin angular momentum of the 3s orbital superimposes negatively with the orbital angular momentum of the 3p orbitals. From Eq. (10.260), $\mathbf{F}_{mag\,2}$ corresponding to the orbital angular momentum of the $3\,p_x$, p_y, and p_z orbitals minus the contribution from the 3s orbital is

$$\mathbf{F}_{mag\,2} = (1+1+1-1)\frac{1}{Z}\frac{\hbar^2}{m_e r_{15}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{2\hbar^2}{m_e r_{15}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.314)$$

The outward centrifugal force on electron 15 is balanced by the electric force and the magnetic forces (on electron 15). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.312)), diamagnetic (Eq. (10.313)), and paramagnetic (Eq. (10.314)) forces as follows:

$$\frac{m_e v_{15}^2}{r_{15}} = \frac{(Z-14)e^2}{4\pi\varepsilon_o r_{15}^2} - \frac{5\hbar^2}{12m_e r_{15}^2 r_{12}}\sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_{15}^2 r_{12}}\sqrt{s(s+1)} \qquad (10.315)$$

Substitution of $v_{15} = \dfrac{\hbar}{m_e r_{15}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.315) gives:

$$\frac{\hbar^2}{m_e r_{15}^3} = \frac{(Z-14)e^2}{4\pi\varepsilon_o r_{15}^2} - \frac{5\hbar^2}{12m_e r_{15}^2 r_{12}}\sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_{15}^2 r_{12}}\sqrt{\frac{3}{4}} \qquad (10.316)$$

$$r_{15} = \frac{\dfrac{\hbar^2}{m_e}}{\dfrac{(Z-14)e^2}{4\pi\varepsilon_o} - \dfrac{5\hbar^2}{12m_e r_{12}}\sqrt{\dfrac{3}{4}} + \dfrac{2\hbar^2}{Zm_e r_{12}}\sqrt{\dfrac{3}{4}}} \qquad (10.317)$$

$$r_{15} = \frac{a_0}{(Z-14)-\left(\dfrac{5}{12}-\dfrac{2}{Z}\right)\dfrac{\sqrt{\dfrac{3}{4}}}{r_{12}}}, \; r_{12} \text{ in units of } a_0 \qquad (10.318)$$

Substitution of $\dfrac{r_{12}}{a_0} = 1.09443$ (Eq. (10.255) with $Z=15$) into Eq. (10.318) gives

$$r_{15} = 1.28900 a_0 \qquad (10.319)$$

The ionization energy of the phosphorous atom is given by the electric energy, $E(electric)$, (Eq. (10.102) with the radius, r_{15}, given by Eq.

(10.319)):

$$E(ionization; P) = -Electric\ Energy = \frac{(Z-14)e^2}{8\pi\varepsilon_o r_{15}} = 10.5554\ eV \qquad (10.320)$$

where $r_{15} = 1.28900a_0$ (Eq. (10.319)) and $Z = 15$. The experimental ionization energy of the phosphorous atom is $10.48669\ eV$ [3].

THE IONIZATION ENERGIES OF FIFTEEN-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>15

Fifteen-electron atoms having $Z > 15$ possess an external electric field given by Eq. (10.92). In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that $\mathbf{F}_{diamagnetic}$ is minimized while $\mathbf{F}_{mag\,2}$ is maximized. With a half-filled 3p shell, the diamagnetic force due to the orbital angular momenta of the 3p electrons cancels that of the 2p electrons. Thus, the diamagnetic force (Eq. (10.258)), $\mathbf{F}_{diamagnetic}$, is zero:

$$\mathbf{F}_{diamagnetic} = 0 \qquad (10.321)$$

From Eqs. (10.205) and (10.261), $\mathbf{F}_{mag\,2}$ corresponding to the spin and orbital angular momenta of the paired $2p_x$, p_y, and p_z electrons is

$$\mathbf{F}_{mag\,2} = (4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_e r_{15}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_{15}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.322)$$

and the contribution from the 3p level is

$$\mathbf{F}_{mag\,2} = (4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_e r_{15}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_{15}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.323)$$

corresponding to the $3p_x$, p_y, and p_z electrons. Thus, the total of $\mathbf{F}_{mag\,2}$ is

$$\mathbf{F}_{mag\,2} = \frac{1}{Z}\frac{24\hbar^2}{m_e r_{15}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.324)$$

The diamagnetic force, $\mathbf{F}_{diamagnetic\,2}$, due to the binding of the 3p-orbital electron having an electric field outside of its radius is given by Eq. (10.268):

$$\mathbf{F}_{diamagnetic\,2} = -\left[\frac{Z-15}{Z-14}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{15}^4}10\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.325)$$

In the case that $Z > 15$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.312)), diamagnetic (Eqs. (10.321) and (10.325)), and paramagnetic (Eq. (10.324)) forces as follows:

$$\frac{m_e v_{15}^2}{r_{15}} = \frac{(Z-14)e^2}{4\pi\varepsilon_o r_{15}^2} + \frac{24\hbar^2}{Z m_e r_{15}^2 r_{12}}\sqrt{s(s+1)} - \left[\frac{Z-15}{Z-14}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{15}^4}10\sqrt{s(s+1)}$$

$$(10.326)$$

Substitution of $v_{15} = \dfrac{\hbar}{m_e r_{15}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.326) gives:

$$\frac{\hbar^2}{m_e r_{15}^3} = \frac{(Z-14)e^2}{4\pi\varepsilon_o r_{15}^2} + \frac{24\hbar^2}{Zm_e r_{15}^2 r_{12}}\sqrt{\frac{3}{4}} - \left[\frac{Z-15}{Z-14}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{15}^4}10\sqrt{\frac{3}{4}}$$

(10.327)

The quadratic equation corresponding to Eq. (10.327) is

$$\left(\frac{(Z-14)e^2}{4\pi\varepsilon_o} + \frac{24\hbar^2}{Zm_e r_{12}}\sqrt{\frac{3}{4}}\right)r_{15}^2 - \frac{\hbar^2}{m_e}r_{15} - \left[\frac{Z-15}{Z-14}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e}10\sqrt{\frac{3}{4}} = 0$$

(10.328)

$$r_{15}^2 - \frac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-14)e^2}{4\pi\varepsilon_o} + \dfrac{24\hbar^2}{Zm_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}r_{15} - \frac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-15}{Z-14}\right]\left(1 - \dfrac{\sqrt{2}}{2} + \dfrac{1}{2}\right)r_{12}10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-14)e^2}{4\pi\varepsilon_o} - \dfrac{24\hbar^2}{Zm_e r_{12}}\sqrt{\dfrac{3}{4}}\right)} = 0$$

(10.329)

The solution of Eq. (10.329) using the quadratic formula is:

$$r_{15} = \frac{\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-14)e^2}{4\pi\varepsilon_o} + \dfrac{24\hbar^2}{Zm_e r_{12}}\sqrt{\dfrac{3}{4}}\right)} \pm \sqrt{\left(\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-14)e^2}{4\pi\varepsilon_o} + \dfrac{24\hbar^2}{Zm_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}\right)^2 + 4\dfrac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-15}{Z-14}\right]\left(1 - \dfrac{\sqrt{2}}{2} + \dfrac{1}{2}\right)r_{12}10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-14)e^2}{4\pi\varepsilon_o} + \dfrac{24\hbar^2}{Zm_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}}}{2}$$

(10.330)

$$r_{15} = \frac{\dfrac{a_0}{\left((Z-14) - \dfrac{12\sqrt{3}}{Zr_{12}}\right)} \pm a_0\sqrt{\left(\dfrac{1}{\left((Z-14) + \dfrac{12\sqrt{3}}{Zr_{12}}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\dfrac{Z-15}{Z-14}\right]\left(1 - \dfrac{\sqrt{2}}{2} + \dfrac{1}{2}\right)r_{12}\right)}{\left((Z-14) - \dfrac{12\sqrt{3}}{Zr_{12}}\right)}}}{2}$$

(10.331)

r_{12} in units of a_0

where r_{12} is given by Eq. (10.255). The positive root of Eq. (10.331) must

be taken in order that $r_{15} > 0$. The final radius of electron 15, r_{15}, is given by Eq. (10.331); this is also the final radius of electrons 13 and 14. The radii of several fifteen-electron atoms are given in Table 10.14.

The ionization energies for the fifteen-electron atoms with $Z > 15$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii r_{15}, given by Eq. (10.331)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-14)e^2}{8\pi\varepsilon_o r_{15}}$$ (10.332)

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured fifteen-electron atoms are given in Table 10.14.

Table 10.14. Ionization energies for some fifteen-electron atoms.

15 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_{10} (a_o) [c]	r_{12} (a_o) [d]	r_{15} (a_o) [e]	Theoretical Ionization Energies [f] (eV)	Experimental Ionization Energies [g] (eV)	Relative Error [h]
P	15	0.06730	0.29010	0.37120	1.09443	1.28900	10.55536	10.48669	-0.0065
S^+	16	0.06306	0.27053	0.33902	0.96729	1.15744	23.5102	23.3379	-0.0074
Cl^{2+}	17	0.05932	0.25344	0.31190	0.86545	1.06759	38.2331	39.61	0.0348
Ar^{3+}	18	0.05599	0.23839	0.28878	0.78276	0.95423	57.0335	59.81	0.0464
K^{4+}	19	0.05302	0.22503	0.26884	0.71450	0.85555	79.5147	82.66	0.0381
Ca^{5+}	20	0.05035	0.21308	0.25149	0.65725	0.77337	105.5576	108.78	0.0296
Sc^{6+}	21	0.04794	0.20235	0.23625	0.60857	0.70494	135.1046	138.0	0.0210
Ti^{7+}	22	0.04574	0.19264	0.22276	0.56666	0.64743	168.1215	170.4	0.0134
V^{8+}	23	0.04374	0.18383	0.21074	0.53022	0.59854	204.5855	205.8	0.0059
Cr^{9+}	24	0.04191	0.17579	0.19995	0.49822	0.55652	244.4799	244.4	-0.0003
Mn^{10+}	25	0.04022	0.16842	0.19022	0.46990	0.52004	287.7926	286.0	-0.0063
Fe^{11+}	26	0.03867	0.16165	0.18140	0.44466	0.48808	334.5138	330.8	-0.0112
Co^{12+}	27	0.03723	0.15540	0.17336	0.42201	0.45985	384.6359	379	-0.0149
Ni^{13+}	28	0.03589	0.14961	0.16601	0.40158	0.43474	438.1529	430	-0.0190
Cu^{14+}	29	0.03465	0.14424	0.15926	0.38305	0.41225	495.0596	484	-0.0229
Zn^{15+}	30	0.03349	0.13925	0.15304	0.36617	0.39199	555.3519	542	-0.0246

[a] Radius of the paired 1s inner electrons of fifteen-electron atoms from Eq. (10.51).

[b] Radius of the paired 2s inner electrons of fifteen-electron atoms from Eq. (10.62).

[c] Radius of the three sets of paired 2p inner electrons of fifteen-electron atoms from Eq. (10.212)).

[d] Radius of the paired 3s inner electrons of fifteen-electron atoms from Eq. (10.255)).

[e] Radius of the three unpaired 3p outer electrons of fifteen-electron atoms from Eq. (10.331) for $Z > 15$ and Eq. (10.319) for P.

[f] Calculated ionization energies of fifteen-electron atoms given by the electric energy (Eq. (10.332)).

[g] From theoretical calculations, interpolation of isoelectronic and spectral series, and

experimental data [2-3].

ᵇ (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.14 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy.   In this case, the experimental capability is three to four significant figures which is consistent with the last column.   The phosphorous atom isoelectronic series is given in Table 10.14 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone.   Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of P isoelectronic and Rydberg series, as well as direct experimental data.

SIXTEEN-ELECTRON ATOMS

Sixteen-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, seven, eight, nine, ten, eleven, twelve, thirteen, fourteen, and fifteen-electron atoms.

RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE SULFUR ATOM

For each fifteen-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), three sets of paired electrons in an orbitsphere at r_{10} given by Eq. (10.212), two indistinguishable spin-paired electrons in an orbitsphere with radii r_{11} and r_{12} both given by Eq. (10.255), and three unpaired electrons in an orbitsphere with radius r_{15} given by Eq. (10.331).   For $Z \geq 16$, the next electron which binds to form the corresponding sixteen-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic forces due to the 3 sets of spin-paired inner 2p electrons and two spin-paired inner 3s electrons.   A paramagnetic spin-paring force to form a filled s orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (7.15) with the radius r_{16}) reduces the energy of the atom less than that due to the alternative forces on a set of paired and two unpaired 3p electrons in an orbitsphere at the same radius r_{16}.   The resulting electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^4$, and the orbital

arrangement is
3p state

$$\underline{\uparrow \downarrow} \quad \underline{\uparrow} \quad \underline{\uparrow} \qquad\qquad (10.333)$$
$$1 \qquad 0 \quad -1$$

corresponding to the ground state $^3P_2$.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner fifteen electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-15)e^2}{4\pi\varepsilon_o r_{16}^2} \mathbf{i}_r \qquad\qquad (10.334)$$

for $r > r_{15}$.

The diamagnetic force, $\mathbf{F}_{diamagnetic}$, is only due to 3p and 3s electrons when the 3p shell is at least half filled since the induced charge-density waves only involve the inner-most shell, the 3s orbital. The energy is minimized with conservation of angular momentum when the induced orbital angular momentum of the 3s orbital superimposes positively with the orbital angular momenta of the other $3p_x$ and the $3p_z$-orbital electrons and the orbital angular momentum of one of the spin-paired $3p_x$ electrons is canceled by the $3p_y$ electron. Thus, $\mathbf{F}_{diamagnetic}$, is given by Eq. (10.258) as the sum of the contributions from the $3p_x$ and p_z orbitals corresponding to $m = 1$ and 0, respectively, and the induced contribution from the 3s orbital corresponding to $m = 0$:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}+\frac{1}{3}+\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_{16}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{4}{3}\right)\frac{\hbar^2}{4m_e r_{16}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.335)$$

The energy is minimized with conservation of angular momentum when the spin angular momentum the 3s orbital superimposes negatively with the spin angular momentum of the $3p_x$ orbital-electron and the orbital angular momentum of the $3p_z$-orbital electron. From Eq. (10.260), $\mathbf{F}_{mag\,2}$ corresponding to the orbital angular momentum of the $3p_x$, p_y, and p_z orbitals minus the contribution from the 3s orbital is

$$\mathbf{F}_{mag\,2} = (1+1-1)\frac{1}{Z}\frac{\hbar^2}{m_e r_{16}^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{\hbar^2}{m_e r_{16}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.336)$$

The outward centrifugal force on electron 16 is balanced by the electric force and the magnetic forces (on electron 16). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.334)), diamagnetic (Eq. (10.335)), and paramagnetic (Eq. (10.336)) forces as follows:

$$\frac{m_e v_{16}^2}{r_{16}} = \frac{(Z-15)e^2}{4\pi\varepsilon_o r_{16}^2} - \frac{4\hbar^2}{12m_e r_{16}^2 r_{12}}\sqrt{s(s+1)} + \frac{\hbar^2}{Zm_e r_{16}^2 r_{12}}\sqrt{s(s+1)} \qquad (10.337)$$

Substitution of $v_{16} = \dfrac{\hbar}{m_e r_{16}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.337) gives:

$$\frac{\hbar^2}{m_e r_{16}^3} = \frac{(Z-15)e^2}{4\pi\varepsilon_o r_{16}^2} - \frac{4\hbar^2}{12 m_e r_{16}^2 r_{12}}\sqrt{\frac{3}{4}} + \frac{\hbar^2}{Z m_e r_{16}^2 r_{12}}\sqrt{\frac{3}{4}} \tag{10.338}$$

$$r_{16} = \frac{\dfrac{\hbar^2}{m_e}}{\dfrac{(Z-15)e^2}{4\pi\varepsilon_o} - \dfrac{4\hbar^2}{12 m_e r_{12}}\sqrt{\dfrac{3}{4}} + \dfrac{\hbar^2}{Z m_e r_{12}}\sqrt{\dfrac{3}{4}}} \tag{10.339}$$

$$r_{16} = \frac{a_0}{(Z-15) - \left(\dfrac{4}{12} - \dfrac{1}{Z}\right)\dfrac{\sqrt{\dfrac{3}{4}}}{r_{12}}}, \; r_{12} \text{ in units of } a_0 \tag{10.340}$$

Substitution of $\dfrac{r_{12}}{a_0} = 0.96729$ (Eq. (10.255) with $Z = 16$) into Eq. (10.340) gives

$$r_{16} = 1.32010 a_0 \tag{10.341}$$

The ionization energy of the sulfur atom is given by the electric energy, $E(electric)$, (Eq. (10.102) with the radius, r_{16}, given by Eq. (10.341)):

$$E(ionization; \; S) = -Electric \; Energy = \frac{(Z-15)e^2}{8\pi\varepsilon_o r_{16}} = 10.30666 \; eV \tag{10.342}$$

where $r_{16} = 1.32010 a_0$ (Eq. (10.341)) and $Z = 16$. The experimental ionization energy of the sulfur atom is $10.36001 \, eV$ [3].

THE IONIZATION ENERGIES OF SIXTEEN-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>16

Sixteen-electron atoms having $Z > 16$ possess an external electric field given by Eq. (10.92). In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that $\mathbf{F}_{diamagnetic}$ is minimized while $\mathbf{F}_{mag\,2}$ is maximized. With a half-filled 3p shell, the diamagnetic force due to the orbital angular momenta of the 3p electrons cancels that of the 2p electrons. Thus, $\mathbf{F}_{diamagnetic}$ is minimized by the formation of a charge-density wave in the 3s orbital corresponding to $m = 1$ in Eq. (10.258) that cancels the orbital angular momentum of one of the $3p_x$ electrons to form the equivalent of a half-filled 3p shell. Then, the contribution due to the 2p level is canceled. From Eq. (10.82), the diamagnetic force, $\mathbf{F}_{diamagnetic}$, is given by the sum of the contributions from the $3p_y$ and p_z orbitals corresponding to $m = -1$ and 0, respectively, and the negative contribution due to the charge-density wave with $m = 1$ induced in the 3s orbital (Eq. (10.258)):

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3} + \frac{1}{3} - \frac{2}{3}\right)\frac{\hbar^2}{4m_e r_{16}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_{16}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.343)$$

From Eq. (10.261), $\mathbf{F}_{mag\,2}$ corresponding to the spin and orbital angular momenta of the paired $2p_x$, p_y, and p_z electrons is

$$\mathbf{F}_{mag\,2} = (4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_e r_{16}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_{16}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.344)$$

and the contribution from the 3p level is

$$\mathbf{F}_{mag\,2} = (8+4+4-4)\frac{1}{Z}\frac{\hbar^2}{m_e r_{16}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_{16}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.345)$$

corresponding to the $3p_x$ (Eq. (10.264)) and p_z (Eq. (10.263)) electrons wherein the contribution due to the $3p_x$ ($m = 1$) electron is canceled by the mirror charge-density wave with $m = 1$ induced in the 3s orbital (Eq. (10.262)). Thus, the total of $\mathbf{F}_{mag\,2}$ is

$$\mathbf{F}_{mag\,2} = \frac{1}{Z}\frac{24\hbar^2}{m_e r_{16}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.346)$$

The diamagnetic force, $\mathbf{F}_{diamagnetic\,2}$, due to the binding of the 3p-orbital electron having an electric field outside of its radius is given by Eq. (10.268):

$$\mathbf{F}_{diamagnetic\,2} = -\left[\frac{Z-16}{Z-15}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{16}^4}10\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.347)$$

In the case that $Z > 16$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.334)), diamagnetic (Eqs. (10.343) and (10.347)), and paramagnetic (Eq. (10.346)) forces as follows:

$$\frac{m_e v_{16}^2}{r_{16}} = \frac{(Z-15)e^2}{4\pi\varepsilon_o r_{16}^2} - \frac{\hbar^2}{12m_e r_{16}^2 r_{12}}\sqrt{s(s+1)} + \frac{24\hbar^2}{Zm_e r_{16}^2 r_{12}}\sqrt{s(s+1)}$$

$$- \left[\frac{Z-16}{Z-15}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{16}^4}10\sqrt{s(s+1)} \qquad (10.348)$$

Substitution of $v_{16} = \dfrac{\hbar}{m_e r_{16}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.348) gives:

$$\frac{\hbar^2}{m_e r_{16}^3} = \frac{(Z-15)e^2}{4\pi\varepsilon_o r_{16}^2} - \frac{\hbar^2}{12m_e r_{16}^2 r_{12}}\sqrt{\frac{3}{4}} + \frac{24\hbar^2}{Zm_e r_{16}^2 r_{12}}\sqrt{\frac{3}{4}} - \left[\frac{Z-16}{Z-15}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{16}^4}10\sqrt{\frac{3}{4}} \qquad (10.349)$$

The quadratic equation corresponding to Eq. (10.349) is

$$\left(\frac{(Z-15)e^2}{4\pi\varepsilon_o} - \left(\frac{1}{12} - \frac{24}{Z}\right)\frac{\hbar^2}{m_e r_{12}}\sqrt{\frac{3}{4}}\right)r_{16}^2 - \frac{\hbar^2}{m_e}r_{16} - \left[\frac{Z-16}{Z-15}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e}10\sqrt{\frac{3}{4}} = 0 \qquad (10.350)$$

$$r_{16}^2 - \cfrac{\cfrac{\hbar^2}{m_e}}{\left(\cfrac{(Z-15)e^2}{4\pi\varepsilon_o}-\left(\cfrac{1}{12}-\cfrac{24}{Z}\right)\cfrac{\hbar^2}{m_e r_{12}}\sqrt{\cfrac{3}{4}}\right)}r_{16} - \cfrac{\cfrac{\hbar^2}{m_e}\left[\cfrac{Z-16}{Z-15}\right]\left(1-\cfrac{\sqrt{2}}{2}+\cfrac{1}{2}\right)r_{12}10\sqrt{\cfrac{3}{4}}}{\left(\cfrac{(Z-15)e^2}{4\pi\varepsilon_o}-\left(\cfrac{1}{12}-\cfrac{24}{Z}\right)\cfrac{\hbar^2}{m_e r_{12}}\sqrt{\cfrac{3}{4}}\right)} = 0$$

$$(10.351)$$

The solution of Eq. (10.351) using the quadratic formula is:

$$r_{16} = \cfrac{\cfrac{\cfrac{\hbar^2}{m_e}}{\left(\cfrac{(Z-15)e^2}{4\pi\varepsilon_o}-\left(\cfrac{1}{12}-\cfrac{24}{Z}\right)\cfrac{\hbar^2}{m_e r_{12}}\sqrt{\cfrac{3}{4}}\right)} \pm \sqrt{\left(\cfrac{\cfrac{\hbar^2}{m_e}}{\left(\cfrac{(Z-15)e^2}{4\pi\varepsilon_o}-\left(\cfrac{1}{12}-\cfrac{24}{Z}\right)\cfrac{\hbar^2}{m_e r_{12}}\sqrt{\cfrac{3}{4}}\right)}\right)^2 + 4\cfrac{\cfrac{\hbar^2}{m_e}\left[\cfrac{Z-16}{Z-15}\right]\left(1-\cfrac{\sqrt{2}}{2}+\cfrac{1}{2}\right)r_{12}10\sqrt{\cfrac{3}{4}}}{\left(\cfrac{(Z-15)e^2}{4\pi\varepsilon_o}-\left(\cfrac{1}{12}-\cfrac{24}{Z}\right)\cfrac{\hbar^2}{m_e r_{12}}\sqrt{\cfrac{3}{4}}\right)}}}{2}$$

$$(10.352)$$

$$r_{16} = \cfrac{\cfrac{a_0}{\left((Z-15)-\left(\cfrac{1}{24}-\cfrac{12}{Z}\right)\cfrac{\sqrt{3}}{r_{12}}\right)} \pm a_0\sqrt{\left(\cfrac{1}{\left((Z-15)-\left(\cfrac{1}{24}-\cfrac{12}{Z}\right)\cfrac{\sqrt{3}}{r_{12}}\right)}\right)^2 + \cfrac{20\sqrt{3}\left(\left[\cfrac{Z-16}{Z-15}\right]\left(1-\cfrac{\sqrt{2}}{2}+\cfrac{1}{2}\right)r_{12}\right)}{\left((Z-15)-\left(\cfrac{1}{24}-\cfrac{12}{Z}\right)\cfrac{\sqrt{3}}{r_{12}}\right)}}}{2}$$

$$(10.353)$$

r_{12} *in units of* a_0

where r_{12} is given by Eq. (10.255). The positive root of Eq. (10.353) must be taken in order that $r_{16} > 0$. The final radius of electron 16, r_{16}, is given by Eq. (10.353); this is also the final radius of electrons 13, 14, and 15. The radii of several sixteen-electron atoms are given in Table 10.15.

The ionization energies for the sixteen-electron atoms with $Z > 16$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii r_{16}, given by Eq. (10.353)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-15)e^2}{8\pi\varepsilon_o r_{16}} \qquad (10.354)$$

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured sixteen-electron atoms are given

in Table 10.15.

Table 10.15. Ionization energies for some sixteen-electron atoms.

16 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_{10} (a_o) [c]	r_{12} (a_o) [d]	r_{16} (a_o) [e]	Theoretical Ionization Energies [f] (eV)	Experimental Ionization Energies [g] (eV)	Relative Error [h]
S	16	0.06306	0.27053	0.33902	0.96729	1.32010	10.30666	10.36001	0.0051
Cl^+	17	0.05932	0.25344	0.31190	0.86545	1.10676	24.5868	23.814	-0.0324
Ar^{2+}	18	0.05599	0.23839	0.28878	0.78276	1.02543	39.8051	40.74	0.0229
K^{3+}	19	0.05302	0.22503	0.26884	0.71450	0.92041	59.1294	60.91	0.0292
Ca^{4+}	20	0.05035	0.21308	0.25149	0.65725	0.82819	82.1422	84.50	0.0279
Sc^{5+}	21	0.04794	0.20235	0.23625	0.60857	0.75090	108.7161	110.68	0.0177
Ti^{6+}	22	0.04574	0.19264	0.22276	0.56666	0.68622	138.7896	140.8	0.0143
V^{7+}	23	0.04374	0.18383	0.21074	0.53022	0.63163	172.3256	173.4	0.0062
Cr^{8+}	24	0.04191	0.17579	0.19995	0.49822	0.58506	209.2996	209.3	0.0000
Mn^{9+}	25	0.04022	0.16842	0.19022	0.46990	0.54490	249.6938	248.3	-0.0056
Fe^{10+}	26	0.03867	0.16165	0.18140	0.44466	0.50994	293.4952	290.2	-0.0114
Co^{11+}	27	0.03723	0.15540	0.17336	0.42201	0.47923	340.6933	336	-0.0140
Ni^{12+}	28	0.03589	0.14961	0.16601	0.40158	0.45204	391.2802	384	-0.0190
Cu^{13+}	29	0.03465	0.14424	0.15926	0.38305	0.42781	445.2492	435	-0.0236
Zn^{14+}	30	0.03349	0.13925	0.15304	0.36617	0.40607	502.5950	490	-0.0257

[a] Radius of the paired 1s inner electrons of sixteen-electron atoms from Eq. (10.51).

[b] Radius of the paired 2s inner electrons of sixteen-electron atoms from Eq. (10.62).

[c] Radius of the three sets of paired 2p inner electrons of sixteen-electron atoms from Eq. (10.212)).

[d] Radius of the paired 3s inner electrons of sixteen-electron atoms from Eq. (10.255)).

[e] Radius of the two paired and two unpaired 3p outer electrons of sixteen-electron atoms from Eq. (10.353) for $Z > 16$ and Eq. (10.341) for S.

[f] Calculated ionization energies of sixteen-electron atoms given by the electric energy (Eq. (10.354)).

[g] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

[h] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.15 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy. In this case, the experimental capability is three to four significant figures which is consistent with the last column. The sulfur atom isoelectronic series is given in Table 10.15 [2-3] to much higher precision than the capability of X-ray spectroscopy, but these values are based on theoretical and interpolation techniques rather than data alone. Ionization energies are difficult to determine since the cut-off

of the Rydberg series of lines at the ionization energy is often not observed, and the ionization energy must be determined from theoretical calculations, interpolation of S isoelectronic and Rydberg series, as well as direct experimental data.

SEVENTEEN-ELECTRON ATOMS

Seventeen-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, seven, eight, nine, ten, eleven, twelve, thirteen, fourteen, fifteen, and sixteen-electron atoms.

RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE CHLORINE ATOM

For each sixteen-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), three sets of paired electrons in an orbitsphere at r_{10} given by Eq. (10.212), two indistinguishable spin-paired electrons in an orbitsphere with radii r_{11} and r_{12} both given by Eq. (10.255), and two paired and two unpaired electrons in an orbitsphere with radius r_{16} given by Eq. (10.353). For $Z \geq 17$, the next electron which binds to form the corresponding seventeen-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic forces due to the 3 sets of spin-paired inner 2p electrons and two spin-paired inner 3s electrons. A paramagnetic spin-paring force to form a filled s orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (7.15) with the radius r_{17}) reduces the energy of the atom less than that due to the alternative forces on two sets of paired electrons and an unpaired 3p electron in an orbitsphere at the same radius r_{17}. The resulting electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^5$, and the orbital arrangement is

3p state

$$\underline{\uparrow \downarrow} \ \underline{\uparrow \downarrow} \ \underline{\uparrow} \qquad\qquad (10.355)$$
$$\ \ 1 \qquad 0 \qquad -1$$

corresponding to the ground state $^2P^0_{3/2}$.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner sixteen electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-16)e^2}{4\pi\varepsilon_o r_{17}^2}\mathbf{i}_r \qquad\qquad (10.356)$$

for $r > r_{16}$.

The diamagnetic force, $\mathbf{F}_{diamagnetic}$, is only due to 3p and 3s electrons when the 3p shell is at least half filled since the induced charge-density waves only involve the inner-most shell, the 3s orbital. Thus, $\mathbf{F}_{diamagnetic}$, is given by Eq. (10.258) as the contribution from the $3p_y$ orbital corresponding to $m = -1$ with the cancellation of the orbital angular momenta of the spin-paired $3p_x$ and p_z electrons:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right)\frac{\hbar^2}{4m_e r_{17}^2 r_{12}}\sqrt{s(s+1)}\,\mathbf{i}_r \tag{10.357}$$

The energy is minimized with conservation of angular momentum when the spin angular momentum of the 3s orbital superimposes negatively with the angular momenta of the 3p orbitals. From Eq. (10.260), $\mathbf{F}_{mag\,2}$ corresponding to the sum of the spin angular momenta of the $3p_x$ and $3p_z$ orbitals and the orbital angular momentum of the $3p_y$ orbital, minus the contribution from the 3s orbital is

$$\mathbf{F}_{mag\,2} = (1+1+1-1)\frac{1}{Z}\frac{\hbar^2}{m_e r_{17}^2 r_{12}}\sqrt{s(s+1)}\,\mathbf{i}_r = \frac{1}{Z}\frac{2\hbar^2}{m_e r_{17}^2 r_{12}}\sqrt{s(s+1)}\,\mathbf{i}_r \tag{10.358}$$

The outward centrifugal force on electron 17 is balanced by the electric force and the magnetic forces (on electron 17). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.356)), diamagnetic (Eq. (10.357)), and paramagnetic (Eq. (10.358)) forces as follows:

$$\frac{m_e v_{17}^2}{r_{17}} = \frac{(Z-16)e^2}{4\pi\varepsilon_o r_{17}^2} - \frac{2\hbar^2}{12m_e r_{17}^2 r_{12}}\sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_{17}^2 r_{12}}\sqrt{s(s+1)} \tag{10.359}$$

Substitution of $v_{17} = \dfrac{\hbar}{m_e r_{17}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.359) gives:

$$\frac{\hbar^2}{m_e r_{17}^3} = \frac{(Z-16)e^2}{4\pi\varepsilon_o r_{17}^2} - \frac{2\hbar^2}{12m_e r_{17}^2 r_{12}}\sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_{17}^2 r_{12}}\sqrt{\frac{3}{4}} \tag{10.360}$$

$$r_{17} = \frac{\dfrac{\hbar^2}{m_e}}{\dfrac{(Z-16)e^2}{4\pi\varepsilon_o} - \dfrac{2\hbar^2}{12m_e r_{12}}\sqrt{\dfrac{3}{4}} + \dfrac{2\hbar^2}{Zm_e r_{12}}\sqrt{\dfrac{3}{4}}} \tag{10.361}$$

$$r_{17} = \frac{a_0}{(Z-16) - \left(\dfrac{2}{12} - \dfrac{2}{Z}\right)\dfrac{\sqrt{\dfrac{3}{4}}}{r_{12}}}, \; r_{12} \text{ in units of } a_0 \tag{10.362}$$

Substitution of $\dfrac{r_{12}}{a_0} = 0.86545$ (Eq. (10.255) with $Z = 17$) into Eq. (10.362) gives

$$r_{17} = 1.05158a_0 \qquad (10.363)$$

The ionization energy of the chlorine atom is given by the electric energy, $E(electric)$, (Eq. (10.102) with the radius, r_{17}, given by Eq. (10.363)):

$$E(ionization;\ Cl) = -Electric\ Energy = \frac{(Z-16)e^2}{8\pi\varepsilon_o r_{17}} = 12.93841\ eV \qquad (10.364)$$

where $r_{17} = 1.05158a_0$ (Eq. (10.363)) and $Z = 17$. The experimental ionization energy of the chlorine atom is $12.96764\ eV$ [3].

THE IONIZATION ENERGIES OF SEVENTEEN-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>17

Seventeen-electron atoms having $Z > 17$ possess an external electric field given by Eq. (10.92). In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that $\mathbf{F}_{diamagnetic}$ is minimized while $\mathbf{F}_{mag\,2}$ is maximized. With a filled 3p shell, the diamagnetic force due to the orbital angular momenta of the 3p electrons cancels that of the 2p electrons. Thus, $\mathbf{F}_{diamagnetic}$ is minimized by the formation of a charge-density wave in the 3s orbital corresponding to two electrons with $m = -1$ in Eq. (10.258) to form the equivalent of a filled 3p level such that the contribution due to the 2p level is canceled. From Eq. (10.82), the diamagnetic force, $\mathbf{F}_{diamagnetic}$, is given by the contribution due to the charge-density wave with $m = -1$ induced in the 3s orbital according to Eq. (10.258):

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right)\frac{\hbar^2}{4m_e r_{17}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.365)$$

From Eqs. (10.205) and (10.261), $\mathbf{F}_{mag\,2}$ corresponding to the spin and orbital angular momenta of the paired $2p_x$, p_y, and p_z electrons is

$$\mathbf{F}_{mag\,2} = (4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_e r_{17}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_{17}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.366)$$

and the contribution from the paired $3p_x$, p_y, and p_z electrons given by Eq. (10.264) is

$$\mathbf{F}_{mag\,2} = (8+8+8)\frac{1}{Z}\frac{\hbar^2}{m_e r_{17}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{24\hbar^2}{m_e r_{17}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.367)$$

wherein the contribution due to the charge-density wave with $m = -1$ induced in the 3s orbital (Eq. (10.262)) provides the equivalent of a filled $3p_y$ orbital and adds a negative contribution of

$$\mathbf{F}_{mag\,2} = -\frac{1}{Z}\frac{4\hbar^2}{m_e r_{17}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.368)$$

Thus, the total of $\mathbf{F}_{mag\,2}$ is

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$$\mathbf{F}_{mag\,2} = \frac{1}{Z}\frac{32\hbar^2}{m_e r_{17}^2 r_{12}}\sqrt{s(s+1)}\,\mathbf{i}_r \tag{10.369}$$

The diamagnetic force, $\mathbf{F}_{diamagnetic\,2}$, due to the binding of the 3p-orbital electron having an electric field outside of its radius is given by Eq. (10.268):

$$\mathbf{F}_{diamagnetic\,2} = -\left[\frac{Z-17}{Z-16}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{17}^4}10\sqrt{s(s+1)}\,\mathbf{i}_r \tag{10.370}$$

In the case that $Z>17$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.356)), diamagnetic (Eqs. (10.365) and (10.370)), and paramagnetic (Eq. (10.369)) forces as follows:

$$\frac{m_e v_{17}^2}{r_{17}} = \frac{(Z-16)e^2}{4\pi\varepsilon_o r_{17}^2} - \frac{2\hbar^2}{12m_e r_{17}^2 r_{12}}\sqrt{s(s+1)} + \frac{32\hbar^2}{Zm_e r_{17}^2 r_{12}}\sqrt{s(s+1)}$$

$$-\left[\frac{Z-17}{Z-16}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{17}^4}10\sqrt{s(s+1)} \tag{10.371}$$

Substitution of $v_{17} = \dfrac{\hbar}{m_e r_{17}}$ (Eq. (1.56)) and $s=\dfrac{1}{2}$ into Eq. (10.371) gives:

$$\frac{\hbar^2}{m_e r_{17}^3} = \frac{(Z-16)e^2}{4\pi\varepsilon_o r_{17}^2} - \frac{2\hbar^2}{12m_e r_{17}^2 r_{12}}\sqrt{\frac{3}{4}} + \frac{32\hbar^2}{Zm_e r_{17}^2 r_{12}}\sqrt{\frac{3}{4}} - \left[\frac{Z-17}{Z-16}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{17}^4}10\sqrt{\frac{3}{4}} \tag{10.372}$$

The quadratic equation corresponding to Eq. (10.372) is

$$\left(\frac{(Z-16)e^2}{4\pi\varepsilon_o} - \left(\frac{2}{12}-\frac{32}{Z}\right)\frac{\hbar^2}{m_e r_{12}}\sqrt{\frac{3}{4}}\right)r_{17}^2 - \frac{\hbar^2}{m_e}r_{17} - \left[\frac{Z-17}{Z-16}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e}10\sqrt{\frac{3}{4}} = 0 \tag{10.373}$$

$$r_{17}^2 - \frac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-16)e^2}{4\pi\varepsilon_o}-\left(\dfrac{2}{12}-\dfrac{32}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}r_{17} - \frac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-17}{Z-16}\right]\left(1-\dfrac{\sqrt{2}}{2}+\dfrac{1}{2}\right)r_{12}10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-16)e^2}{4\pi\varepsilon_o}-\left(\dfrac{2}{12}-\dfrac{32}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)} = 0 \tag{10.374}$$

The solution of Eq. (10.374) using the quadratic formula is:

$$r_{17} = \frac{\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-16)e^2}{4\pi\varepsilon_o} - \left(\dfrac{2}{12} - \dfrac{32}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)} \pm \sqrt{\left(\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-16)e^2}{4\pi\varepsilon_o} - \left(\dfrac{2}{12} - \dfrac{32}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}\right)^2 + 4\dfrac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-17}{Z-16}\right]\left(1 - \dfrac{\sqrt{2}}{2} + \dfrac{1}{2}\right)r_{12}10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-16)e^2}{4\pi\varepsilon_o} - \left(\dfrac{2}{12} - \dfrac{32}{Z}\right)\dfrac{\hbar^2}{m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}}}{2}$$

(10.375)

$$r_{17} = \frac{\dfrac{a_0}{\left((Z-16) - \left(\dfrac{1}{12} - \dfrac{16}{Z}\right)\dfrac{\sqrt{3}}{r_{12}}\right)} \pm a_0 \sqrt{\left(\dfrac{1}{\left((Z-16) - \left(\dfrac{1}{12} - \dfrac{16}{Z}\right)\dfrac{\sqrt{3}}{r_{12}}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\dfrac{Z-17}{Z-16}\right]\left(1 - \dfrac{\sqrt{2}}{2} + \dfrac{1}{2}\right)r_{12}\right)}{\left((Z-16) - \left(\dfrac{1}{12} - \dfrac{16}{Z}\right)\dfrac{\sqrt{3}}{r_{12}}\right)}}}{2}$$

(10.376)

r_{12} in units of a_0

where r_{12} is given by Eq. (10.255). The positive root of Eq. (10.376) must be taken in order that $r_{17} > 0$. The final radius of electron 17, r_{17}, is given by Eq. (10.376); this is also the final radius of electrons 13, 14, 15, and 16.   The radii of several seventeen-electron atoms are given in Table 10.16.

The ionization energies for the seventeen-electron atoms with $Z > 17$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii r_{17}, given by Eq. (10.376)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-16)e^2}{8\pi\varepsilon_o r_{17}}$$

(10.377.)

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured seventeen-electron atoms are given in Table 10.16.

Table 10.16. Ionization energies for some seventeen-electron atoms.

17 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_{10} (a_o) [c]	r_{12} (a_o) [d]	r_{17} (a_o) [e]	Theoretical Ionization Energies [f] (eV)	Experimental Ionization Energies [g] (eV)	Relative Error [h]
Cl	17	0.05932	0.25344	0.31190	0.86545	1.05158	12.93841	12.96764	0.0023
Ar^+	18	0.05599	0.23839	0.28878	0.78276	0.98541	27.6146	27.62967	0.0005
K^{2+}	19	0.05302	0.22503	0.26884	0.71450	0.93190	43.8001	45.806	0.0438
Ca^{3+}	20	0.05035	0.21308	0.25149	0.65725	0.84781	64.1927	67.27	0.0457
Sc^{4+}	21	0.04794	0.20235	0.23625	0.60857	0.77036	88.3080	91.65	0.0365
Ti^{5+}	22	0.04574	0.19264	0.22276	0.56666	0.70374	116.0008	119.53	0.0295
V^{6+}	23	0.04374	0.18383	0.21074	0.53022	0.64701	147.2011	150.6	0.0226
Cr^{7+}	24	0.04191	0.17579	0.19995	0.49822	0.59849	181.8674	184.7	0.0153
Mn^{8+}	25	0.04022	0.16842	0.19022	0.46990	0.55667	219.9718	221.8	0.0082
Fe^{9+}	26	0.03867	0.16165	0.18140	0.44466	0.52031	261.4942	262.1	0.0023
Co^{10+}	27	0.03723	0.15540	0.17336	0.42201	0.48843	306.4195	305	-0.0047
Ni^{11+}	28	0.03589	0.14961	0.16601	0.40158	0.46026	354.7360	352	-0.0078
Cu^{12+}	29	0.03465	0.14424	0.15926	0.38305	0.43519	406.4345	401	-0.0136
Zn^{13+}	30	0.03349	0.13925	0.15304	0.36617	0.41274	461.5074	454	-0.0165

[a] Radius of the paired 1s inner electrons of seventeen-electron atoms from Eq. (10.51).
[b] Radius of the paired 2s inner electrons of seventeen-electron atoms from Eq. (10.62).
[c] Radius of the three sets of paired 2p inner electrons of seventeen-electron atoms from Eq. (10.212)).
[d] Radius of the paired 3s inner electrons of seventeen-electron atoms from Eq. (10.255)).
[e] Radius of the two sets of paired and an unpaired 3p outer electron of seventeen-electron atoms from Eq. (10.376) for $Z > 17$ and Eq. (10.363) for Cl.
[f] Calculated ionization energies of seventeen-electron atoms given by the electric energy (Eq. (10.377)).
[g] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].
[h] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.16 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy. In this case, the experimental capability is about two to four significant figures which is consistent with the last column. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed. Thus, the chlorine atom isoelectronic series given in Table 10.16 [2-3] relies on theoretical calculations and interpolation of the Cl isoelectronic and Rydberg series as well as direct experimental data to extend the precision beyond the capability of X-ray spectroscopy. But, no assurances can be given that these techniques are correct, and they may not improve

the results.   The error given in the last column is very reasonable given the quality of the data.

EIGHTEEN-ELECTRON ATOMS

Eighteen-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, seven, eight, nine, ten, eleven, twelve, thirteen, fourteen, fifteen, sixteen, and seventeen-electron atoms.

RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE ARGON ATOM

For each seventeen-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), three sets of paired electrons in an orbitsphere at r_{10} given by Eq. (10.212), two indistinguishable spin-paired electrons in an orbitsphere with radii r_{11} and r_{12} both given by Eq. (10.255), and two sets of paired and an unpaired electron in an orbitsphere with radius r_{17} given by Eq. (10.376). For $Z \geq 18$, the next electron which binds to form the corresponding eighteen-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic forces due to the 3 sets of spin-paired inner 2p electrons and two spin-paired inner 3s electrons.   A paramagnetic spin-paring force to form a filled s orbital is also possible, but the force due to the spin-pairing of the electrons (Eq. (7.15) with the radius r_{18}) reduces the energy of the atom less than that due to the alternative forces on three sets of paired 3p electrons in an orbitsphere at the same radius r_{18}. The resulting electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^6$, and the orbital arrangement is

3p state

$$\underline{\uparrow \downarrow} \ \underline{\uparrow \downarrow} \ \underline{\uparrow \downarrow} \qquad\qquad (10.378)$$
$$\quad 1 \qquad 0 \qquad -1$$

corresponding to the ground state $^1S_0$.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner seventeen electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-17)e^2}{4\pi\varepsilon_o r_{18}^2} \mathbf{i}_r \qquad\qquad (10.379)$$

for $r > r_{17}$.

As in the case on the neon atom, the energy of the argon atom is minimized and the angular momentum is conserved with the pairing of electron eighteen to fill the $3p_y$ orbital when the orbital angular momenta of each set of the $3p_x$, p_y, and p_z spin-paired electrons adds negatively to cancel. Then, the diamagnetic force (Eq. (10.258)), $\mathbf{F}_{diamagnetic}$, is given by the induced orbital angular momentum of the 3s orbital alone which conserves angular momentum.

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_{18}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.380)$$

From Eq. (10.260), $\mathbf{F}_{mag\,2}$ is

$$\mathbf{F}_{mag\,2} = (1+1+1+1)\frac{1}{Z}\frac{\hbar^2}{m_e r_{18}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{4\hbar^2}{m_e r_{18}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.381)$$

corresponding to the spin-angular-momentum contribution alone from each of the $3p_x$, p_y, and p_z orbitals and the spin angular momentum of the 3s orbital.

The outward centrifugal force on electron 18 is balanced by the electric force and the magnetic forces (on electron 18). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.379)), diamagnetic (Eq. (10.380)), and paramagnetic (Eq. (10.381)) forces as follows:

$$\frac{m_e v_{18}^2}{r_{18}} = \frac{(Z-17)e^2}{4\pi\varepsilon_o r_{18}^2} - \frac{\hbar^2}{12m_e r_{18}^2 r_{12}}\sqrt{s(s+1)} + \frac{4\hbar^2}{Zm_e r_{18}^2 r_{12}}\sqrt{s(s+1)} \qquad (10.382)$$

Substitution of $v_{18} = \dfrac{\hbar}{m_e r_{18}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.382) gives:

$$\frac{\hbar^2}{m_e r_{18}^3} = \frac{(Z-17)e^2}{4\pi\varepsilon_o r_{18}^2} - \frac{\hbar^2}{12m_e r_{18}^2 r_{12}}\sqrt{\frac{3}{4}} + \frac{4\hbar^2}{Zm_e r_{18}^2 r_{12}}\sqrt{\frac{3}{4}} \qquad (10.383)$$

$$r_{18} = \frac{\dfrac{\hbar^2}{m_e}}{\dfrac{(Z-17)e^2}{4\pi\varepsilon_o} - \dfrac{\hbar^2}{12m_e r_{12}}\sqrt{\dfrac{3}{4}} + \dfrac{4\hbar^2}{Zm_e r_{12}}\sqrt{\dfrac{3}{4}}} \qquad (10.384)$$

$$r_{18} = \frac{a_0}{(Z-17) - \left(\dfrac{1}{12} - \dfrac{4}{Z}\right)\dfrac{\sqrt{\dfrac{3}{4}}}{r_{12}}}, \; r_{12} \text{ in units of } a_0 \qquad (10.385)$$

Substitution of $\dfrac{r_{12}}{a_0} = 0.78276$ (Eq. (10.255) with $Z = 18$) into Eq. (10.385) gives

$$r_{18} = 0.86680a_0 \qquad (10.386)$$

The ionization energy of the argon atom is given by the electric

energy, $E(electric)$, (Eq. (10.102) with the radius, r_{18}, given by Eq. (10.386)):

$$E(ionization;\ Ar) = -Electric\ Energy = \frac{(Z-17)e^2}{8\pi\varepsilon_o r_{18}} = 15.69651\ eV \qquad (10.387)$$

where $r_{18} = 0.86680a_0$ (Eq. (10.386)) and $Z = 18$.   The experimental ionization energy of the argon atom is $15.75962\ eV$ [3].

THE IONIZATION ENERGIES OF EIGHTEEN-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>18

Eighteen-electron atoms having $Z > 18$ possess an external electric field given by Eq. (10.92).   In this case, an energy minimum is achieved with conservation of momentum when the orbital angular momentum is such that $\mathbf{F}_{diamagnetic}$ is minimized while $\mathbf{F}_{mag\ 2}$ is maximized.   With a filled 3p shell, the diamagnetic force due to the orbital angular momenta of the 3p electrons cancels that of the 2p electrons.   Thus, the diamagnetic force (Eq. (10.258)), $\mathbf{F}_{diamagnetic}$, is zero:

$$\mathbf{F}_{diamagnetic} = 0 \qquad (10.388)$$

From Eqs. (10.205) and (10.261), $\mathbf{F}_{mag\ 2}$ corresponding to the spin and orbital angular momenta of the paired $2p_x$, p_y, and p_z electrons is

$$\mathbf{F}_{mag\ 2} = (4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_e r_{18}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_{18}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.389)$$

the contribution from the 3p level (Eq. (10.264)) is

$$\mathbf{F}_{mag\ 2} = (8+8+8)\frac{1}{Z}\frac{\hbar^2}{m_e r_{18}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{24\hbar^2}{m_e r_{18}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.390)$$

and the contribution due to the spin and induced orbital angular momentum of the 3s orbital that achieves conservation of angular momentum given by Eq. (10.262) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{4\hbar^2}{m_e r_{18}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.391)$$

Thus, the total of $\mathbf{F}_{mag\ 2}$ is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{40\hbar^2}{m_e r_{18}^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.392)$$

The diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, due to the binding of the 3p-orbital electron having an electric field outside of its radius is given by Eq. (10.268):

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-18}{Z-17}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{18}^4}10\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.393)$$

In the case that $Z > 18$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.379)), diamagnetic (Eqs. (10.388) and (10.393)), and paramagnetic

(Eq. (10.392)) forces as follows:

$$\frac{m_e v_{18}^2}{r_{18}} = \frac{(Z-17)e^2}{4\pi\varepsilon_o r_{18}^2} + \frac{40\hbar^2}{2m_e r_{18}^2 r_{12}}\sqrt{s(s+1)} - \left[\frac{Z-18}{Z-17}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{18}^4}10\sqrt{s(s+1)}$$

(10.394)

Substitution of $v_{18} = \frac{\hbar}{m_e r_{18}}$ (Eq. (1.56)) and $s = \frac{1}{2}$ into Eq. (10.394) gives:

$$\frac{\hbar^2}{m_e r_{18}^3} = \frac{(Z-17)e^2}{4\pi\varepsilon_o r_{18}^2} + \frac{40\hbar^2}{2m_e r_{18}^2 r_{12}}\sqrt{\frac{3}{4}} - \left[\frac{Z-18}{Z-17}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e r_{18}^4}10\sqrt{\frac{3}{4}}$$

(10.395)

The quadratic equation corresponding to Eq. (10.395) is

$$\left(\frac{(Z-17)e^2}{4\pi\varepsilon_o} + \frac{40\hbar^2}{2m_e r_{12}}\sqrt{\frac{3}{4}}\right)r_{18}^2 - \frac{\hbar^2}{m_e}r_{18} - \left[\frac{Z-18}{Z-17}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{12}\hbar^2}{m_e}10\sqrt{\frac{3}{4}} = 0$$

(10.396)

$$r_{18}^2 - \frac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-17)e^2}{4\pi\varepsilon_o} + \dfrac{40\hbar^2}{2m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}r_{18} - \frac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-18}{Z-17}\right]\left(1 - \dfrac{\sqrt{2}}{2} + \dfrac{1}{2}\right)r_{12}10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-17)e^2}{4\pi\varepsilon_o} + \dfrac{40\hbar^2}{2m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)} = 0$$

(10.397)

The solution of Eq. (10.397) using the quadratic formula is:

$$r_{18} = \frac{\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-17)e^2}{4\pi\varepsilon_o} + \dfrac{40\hbar^2}{2m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)} \pm \sqrt{\left(\dfrac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-17)e^2}{4\pi\varepsilon_o} + \dfrac{40\hbar^2}{2m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}\right)^2 + 4\dfrac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-18}{Z-17}\right]\left(1 - \dfrac{\sqrt{2}}{2} + \dfrac{1}{2}\right)r_{12}10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-17)e^2}{4\pi\varepsilon_o} + \dfrac{40\hbar^2}{2m_e r_{12}}\sqrt{\dfrac{3}{4}}\right)}}}{2}$$

(10.398)

$$r_{18} = \cfrac{\cfrac{a_0}{\left((Z-17)+\cfrac{20\sqrt{3}}{Zr_{12}}\right)} \pm a_0 \sqrt{\left(\cfrac{1}{\left((Z-17)+\cfrac{20\sqrt{3}}{Zr_{12}}\right)}\right)^2 + \cfrac{20\sqrt{3}\left(\left[\cfrac{Z-18}{Z-17}\right]\left(1-\cfrac{\sqrt{2}}{2}+\cfrac{1}{2}\right)r_{12}\right)}{\left((Z-17)+\cfrac{20\sqrt{3}}{Zr_{12}}\right)}}}{2}$$

(10.399)

r_{12} *in units of* a_0

where r_{12} is given by Eq. (10.255). The positive root of Eq. (10.399) must be taken in order that $r_{18} > 0$. The final radius of electron 18, r_{18}, is given by Eq. (10.399); this is also the final radius of electrons 13, 14, 15, 16, and 17. The radii of several eighteen-electron atoms are given in Table 10.17.

The ionization energies for the eighteen-electron atoms with $Z > 18$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii r_{18}, given by Eq. (10.399)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-17)e^2}{8\pi\varepsilon_o r_{18}}$$

(10.400)

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured eighteen-electron atoms are given in Table 10.17.

Table 10.17. Ionization energies for some eighteen-electron atoms.

18 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_{10} (a_o) [c]	r_{12} (a_o) [d]	r_{18} (a_o) [e]	Theoretical Ionization Energies [f] (eV)	Experimental Ionization Energies [g] (eV)	Relative Error [h]
Ar	18	0.05599	0.23839	0.28878	0.78276	0.86680	15.69651	15.75962	0.0040
K^+	19	0.05302	0.22503	0.26884	0.71450	0.85215	31.9330	31.63	-0.0096
Ca^{2+}	20	0.05035	0.21308	0.25149	0.65725	0.82478	49.4886	50.9131	0.0280
Sc^{3+}	21	0.04794	0.20235	0.23625	0.60857	0.76196	71.4251	73.4894	0.0281
Ti^{4+}	22	0.04574	0.19264	0.22276	0.56666	0.70013	97.1660	99.30	0.0215
V^{5+}	23	0.04374	0.18383	0.21074	0.53022	0.64511	126.5449	128.13	0.0124
Cr^{6+}	24	0.04191	0.17579	0.19995	0.49822	0.59718	159.4836	160.18	0.0043
Mn^{7+}	25	0.04022	0.16842	0.19022	0.46990	0.55552	195.9359	194.5	-0.0074
Fe^{8+}	26	0.03867	0.16165	0.18140	0.44466	0.51915	235.8711	233.6	-0.0097
Co^{9+}	27	0.03723	0.15540	0.17336	0.42201	0.48720	279.2670	275.4	-0.0140
Ni^{10+}	28	0.03589	0.14961	0.16601	0.40158	0.45894	326.1070	321.0	-0.0159
Cu^{11+}	29	0.03465	0.14424	0.15926	0.38305	0.43379	376.3783	369	-0.0200
Zn^{12+}	30	0.03349	0.13925	0.15304	0.36617	0.41127	430.0704	419.7	-0.0247

[a] Radius of the paired 1s inner electrons of eighteen-electron atoms from Eq. (10.51).

[b] Radius of the paired 2s inner electrons of eighteen-electron atoms from Eq. (10.62).

[c] Radius of the three sets of paired 2p inner electrons of eighteen-electron atoms from Eq. (10.212)).

[d] Radius of the paired 3s inner electrons of eighteen-electron atoms from Eq. (10.255)).

[e] Radius of the three sets of paired 3p outer electrons of eighteen-electron atoms from Eq. (10.399) for $Z > 18$ and Eq. (10.386) for Ar.

[f] Calculated ionization energies of eighteen-electron atoms given by the electric energy (Eq. (10.400)).

[g] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

[h] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.17 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy. In this case, the experimental capability is about two to four significant figures which is consistent with the last column. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed. Thus, the argon atom isoelectronic series given in Table 10.17 [2-3] relies on theoretical calculations and interpolation of the Ar isoelectronic and Rydberg series as well as direct experimental data to extend the precision beyond the capability of X-ray spectroscopy. But, no assurances can be given that these techniques are correct, and they may not improve the results. The error given in the last column is very reasonable given the

quality of the data.

GENERAL EQUATION FOR THE IONIZATION ENERGIES OF THIRTEEN THROUGH EIGHTEEN-ELECTRON ATOMS

Using the forces given by Eqs. (10.257-10.264) (10.268), and the radii r_{12} given by Eq. (10.255), the radii of the 3p electrons of all thirteen through eighteen-electron atoms may be solved exactly. The electric energy given by Eq. (10.102) gives the corresponding exact ionization energies. A summary of the parameters of the equations that determine the exact radii and ionization energies of all thirteen through eighteen-electron atoms is given in Table 10.18.

F_{ele} and $F_{diamagnetic\ 2}$ given by Eqs. (10.257) and (10.268), respectively, are of the same form for all atoms with the appropriate nuclear charges and atomic radii. $F_{diamagnetic}$ given by Eq. (10.258) and $F_{mag\ 2}$ given by Eqs. (10.259-10.264) are of the same form with the appropriate factors that depend on the electron configuration wherein the electron configuration must be a minimum of energy.

For each n-electron atom having a central charge of Z times that of the proton and an electron configuration $1s^2 2s^2 2p^6 3s^2 3p^{n-12}$, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) and (10.51):

$$r_1 = r_2 = a_o \left[\frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)} \right] \tag{10.401}$$

two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62):

$$r_4 = r_3 = \cfrac{\cfrac{a_o\left(1 - \frac{\sqrt{\frac{3}{4}}}{Z}\right)}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)} \pm a_o \sqrt{\cfrac{\left(1 - \frac{\sqrt{\frac{3}{4}}}{Z}\right)^2}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)^2} + 4\cfrac{\left[\frac{Z-3}{Z-2}\right]r_1 10\sqrt{\frac{3}{4}}}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)}}}{2}$$

r_1 in units of a_o

$$\tag{10.402}$$

where r_1 is given by Eqs. (10.51) and (10.401), three sets of paired indistinguishable electrons in an orbitsphere with radius r_{10} given by Eq.

(10.212):

$$r_{10} = \cfrac{\cfrac{a_0}{\left((Z-9)-\left(\cfrac{5}{24}-\cfrac{6}{Z}\right)\cfrac{\sqrt{3}}{r_3}\right)} \pm a_0 \sqrt{\left(\cfrac{1}{\left((Z-9)-\left(\cfrac{5}{24}-\cfrac{6}{Z}\right)\cfrac{\sqrt{3}}{r_3}\right)}\right)^2 + \cfrac{20\sqrt{3}\left(\left[\cfrac{Z-10}{Z-9}\right]\left(1-\cfrac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-9)-\left(\cfrac{5}{24}-\cfrac{6}{Z}\right)\cfrac{\sqrt{3}}{r_3}\right)}}}{2}$$ (10.403)

$$r_3 \text{ in units of } a_0$$

where r_3 is given by Eqs. (10.62) and (10.402), two indistinguishable spin-paired electrons in an orbitsphere with radius r_{12} given by Eq. (10.255):

$$r_{12} = \cfrac{\cfrac{a_0}{\left((Z-11)-\left(\cfrac{1}{8}-\cfrac{3}{Z}\right)\cfrac{\sqrt{3}}{r_{10}}\right)} \pm a_0 \sqrt{\left(\cfrac{1}{\left((Z-11)-\left(\cfrac{1}{8}-\cfrac{3}{Z}\right)\cfrac{\sqrt{3}}{r_{10}}\right)}\right)^2 + \cfrac{20\sqrt{3}\left(\left[\cfrac{Z-12}{Z-11}\right]\left(1+\cfrac{\sqrt{2}}{2}\right)r_{10}\right)}{\left((Z-11)-\left(\cfrac{1}{8}-\cfrac{3}{Z}\right)\cfrac{\sqrt{3}}{r_{10}}\right)}}}{2}$$ (10.404)

$$r_{10} \text{ in units of } a_0$$

where r_{10} is given by Eq. (10.212), and $n-12$ electrons in a 3p orbitsphere with radius r_n given by

$$r_n = \frac{\dfrac{a_0}{\left((Z-(n-1))-\left(\dfrac{A}{8}-\dfrac{B}{2Z}\right)\dfrac{\sqrt{3}}{r_{12}}\right)} \pm a_0 \sqrt{\left(\dfrac{1}{\left((Z-(n-1))-\left(\dfrac{A}{8}-\dfrac{B}{2Z}\right)\dfrac{\sqrt{3}}{r_{12}}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\dfrac{Z-n}{Z-(n-1)}\right]\left(1-\dfrac{\sqrt{2}}{2}+\dfrac{1}{2}\right)r_{12}\right)}{\left((Z-(n-1))-\left(\dfrac{A}{8}-\dfrac{B}{2Z}\right)\dfrac{\sqrt{3}}{r_{12}}\right)}}}{2}$$

(10.405)

r_{12} *in units of* a_0

where r_{12} is given by Eqs. (10.255) and (10.404), the parameter A given in Table 10.18 corresponds to the diamagnetic force, $\mathbf{F}_{diamagnetic}$, (Eq. (10.258)), and the parameter B given in Table 10.18 corresponds to the paramagnetic force, $\mathbf{F}_{mag\,2}$ (Eqs. (10.260-10.264)). The positive root of Eq. (10.405) must be taken in order that $r_n > 0$. The radii of several n-electron 3p atoms are given in Tables 10.10-10.17.

The ionization energy for the aluminum atom is given by Eq. (10.227). The ionization energies for the n-electron 3p atoms are given by the negative of the electric energy, $E(electric)$, (Eq. (10.102) with the radii, r_n, given by Eq. (10.405)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-(n-1))e^2}{8\pi\varepsilon_o r_n}$$

(10.406)

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured n-electron 3p atoms are given by Eqs. (10.405) and (10.406) in Tables 10.10-10.17.

Table 10.18. Summary of the parameters of thirteen through eighteen-electron atoms.

Atom Type	Electron Configuration	Ground State Term [a]	Orbital Arrangement of 3p Electrons (3p state)			Diamagnetic Force Factor A [b]	Paramagnetic Force Factor B [c]
			1	0	-1		
Neutral 13 e Atom Al	$1s^2 2s^2 2p^6 3s^2 3p^1$	$^2P^0_{1/2}$	↑	—	—	$\dfrac{11}{3}$	0
Neutral 14 e Atom Si	$1s^2 2s^2 2p^6 3s^2 3p^2$	$^3P_0$	↑	↑	—	$\dfrac{7}{3}$	0
Neutral 15 e Atom P	$1s^2 2s^2 2p^6 3s^2 3p^3$	$^4S^0_{3/2}$	↑	↑	↑	$\dfrac{5}{3}$	2
Neutral 16 e Atom S	$1s^2 2s^2 2p^6 3s^2 3p^4$	$^3P_2$	↑↓	↑	↑	$\dfrac{4}{3}$	1
Neutral 17 e Atom Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$	$^2P^0_{3/2}$	↑↓	↑↓	↑	$\dfrac{2}{3}$	2
Neutral 18 e Atom Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$	$^1S_0$	↑↓	↑↓	↑↓	$\dfrac{1}{3}$	4
13 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^1$	$^2P^0_{1/2}$	↑	—	—	$\dfrac{5}{3}$	12
14 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^2$	$^3P_0$	↑	↑	—	$\dfrac{1}{3}$	16
15 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^3$	$^4S^0_{3/2}$	↑	↑	↑	0	24
16 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^4$	$^3P_2$	↑↓	↑	↑	$\dfrac{1}{3}$	24
17 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^5$	$^2P^0_{3/2}$	↑↓	↑↓	↑	$\dfrac{2}{3}$	32
18 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^6$	$^1S_0$	↑↓	↑↓	↑↓	0	40

[a] The theoretical ground state terms match those given by NIST [8].
[b] Eq. (10.258).
[c] Eqs. (10.260-10.264).

NINETEEN-ELECTRON ATOMS

Nineteen-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, seven, eight, nine, ten, eleven, twelve, thirteen, fourteen, fifteen, sixteen, seventeen, and eighteen-electron atoms.

RADIUS AND IONIZATION ENERGY OF THE OUTER ELECTRON OF THE POTASSIUM ATOM

For each eighteen-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), three sets of paired electrons in an orbitsphere at r_{10} given by Eq. (10.212), two indistinguishable spin-paired electrons in an orbitsphere with radii r_{11} and r_{12} both given by Eq. (10.255), and three sets of paired electrons in an orbitsphere with radius r_{18} given by Eq. (10.399). For $Z \geq 19$, the next electron which binds to form the corresponding nineteen-electron atom is attracted by the central Coulomb field and is repelled by diamagnetic forces due to the 3 sets of spin-paired inner 3p electrons such that it forms and unpaired orbitsphere at radius r_{19}.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner eighteen electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-18)e^2}{4\pi\varepsilon_o r_{19}^2}\mathbf{i}_r \tag{10.407}$$

for $r > r_{18}$.

The spherically symmetrical closed 3p shell of eighteen-electron atoms produces a diamagnetic force, $\mathbf{F}_{diamagnetic}$, that is equivalent to that of a closed s shell given by Eq. (10.11) with the appropriate radii except that the force is doubled due to the interaction of the 4s and 3p electrons as given by Eq. (10.96). The inner electrons remain at their initial radii, but cause a diamagnetic force according to Lenz's law that is

$$\mathbf{F}_{diamagnetic} = -\frac{2\hbar^2}{4m_e r_{19}^2 r_{18}}\sqrt{s(s+1)}\mathbf{i}_r \tag{10.408}$$

In addition to the spin-spin interaction between electron pairs, the three sets of 3p electrons are orbitally paired. As in the case of the sodium atom with the corresponding radii, the single 4s orbital of the potassium atom produces a magnetic field at the position of the three sets

of spin-paired 3p electrons. In order for the electrons to remain spin and orbitally paired, a corresponding diamagnetic force, $F_{diamagnetic\,3}$, on electron eighteen from the three sets of spin-paired electrons that follows from the deviation given in the Eleven-Electron Atom section (Eq. (10.221)) is

$$F_{diamagnetic\,3} = -\frac{1}{Z}\frac{12\hbar^2}{m_e r_{19}^3}\sqrt{s(s+1)}\,i_r \tag{10.409}$$

corresponding to the $3p_x$, p_y, and p_z electrons.

The outward centrifugal force on electron 19 is balanced by the electric force and the magnetic forces (on electron 19). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.407)) and diamagnetic (Eqs. (10.408) and (10.409)) forces as follows:

$$\frac{m_e v_{19}^2}{r_{19}} = \frac{(Z-18)e^2}{4\pi\varepsilon_o r_{19}^2} - \frac{2\hbar^2}{4m_e r_{19}^2 r_{18}}\sqrt{s(s+1)} - \frac{12\hbar^2}{Zm_e r_{19}^3}\sqrt{s(s+1)} \tag{10.410}$$

Substitution of $v_{19} = \dfrac{\hbar}{m_e r_{19}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.410) gives:

$$\frac{\hbar^2}{m_e r_{19}^3} = \frac{(Z-18)e^2}{4\pi\varepsilon_o r_{19}^2} - \frac{2\hbar^2}{4m_e r_{19}^2 r_{18}}\sqrt{\frac{3}{4}} - \frac{12\hbar^2}{Zm_e r_{19}^3}\sqrt{\frac{3}{4}} \tag{10.411}$$

$$r_{19} = \frac{\dfrac{\hbar^2}{m_e}\left(1 + \dfrac{12}{Z}\sqrt{\dfrac{3}{4}}\right)}{\dfrac{(Z-18)e^2}{4\pi\varepsilon_o} - \dfrac{\hbar^2}{2m_e r_{18}}\sqrt{\dfrac{3}{4}}} \tag{10.412}$$

$$r_{19} = \frac{a_0\left(1 + \dfrac{12}{Z}\sqrt{\dfrac{3}{4}}\right)}{(Z-18) - \dfrac{\sqrt{\dfrac{3}{4}}}{2r_{18}}}, \; r_{18} \text{ in units of } a_0 \tag{10.413}$$

Substitution of $\dfrac{r_{18}}{a_0} = 0.85215$ (Eq. (10.399) with $Z=19$) into Eq. (10.413) gives

$$r_{19} = 3.14515 a_0 \tag{10.414}$$

The ionization energy of the potassium atom is given by the electric energy, $E(electric)$, (Eq. (10.102) with the radius, r_{19}, given by Eq. (10.414)):

$$E(ionization; \, K) = -Electric\,Energy = \frac{(Z-18)e^2}{8\pi\varepsilon_o r_{19}} = 4.32596 \; eV \tag{10.415}$$

where $r_{19} = 3.14515 a_0$ (Eq. (10.414)) and $Z = 19$. The experimental ionization energy of the potassium atom is $4.34066 \; eV$ [3].

THE IONIZATION ENERGIES OF NINETEEN-ELECTRON ATOMS

WITH A NUCLEAR CHARGE Z>19

Nineteen-electron atoms having $Z > 19$ possess an external electric field given by Eq. (10.92). Since there is a source of dissipative, $\mathbf{J} \bullet \mathbf{E}$ of Eq. (10.27), the magnetic moments of the inner electrons may change due to the outer electron such that the energy of the nineteen-electron atom is lowered.   The spherically symmetrical closed 3p shell of eighteen-electron atoms produces a diamagnetic force, $\mathbf{F}_{diamagnetic}$, that is equivalent to that of a closed s shell given by Eq. (10.11) with the appropriate radii except that the force is tripled due to the interaction of the 2p, 3s, and 3p electrons as discussed in the 3P-Orbital Electrons Based on an Energy Minimum section.   The inner electrons remain at their initial radii, but cause a diamagnetic force according to Lenz's law that is

$$\mathbf{F}_{diamagnetic} = -\frac{3\hbar^2}{4m_e r_{19}^2 r_{18}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.416)$$

In addition to the spin-spin interaction between electron pairs, the six sets of 2p and 3p electrons are orbitally paired.   As in given in the Eleven-Electron Atom section, the single 4s orbital of each nineteen-electron atoms having $Z > 19$ produces a magnetic field at the position of the six sets of spin-paired 2p and 3p electrons.   In order for the electrons to remain spin and orbitally paired, a corresponding diamagnetic force, $\mathbf{F}_{diamagnetic\,3}$, on electron nineteen from the six sets of spin-paired electrons that follows from the deviation given in the Eleven-Electron Atom section (Eq. (10.221)) is

$$\mathbf{F}_{diamagnetic\,3} = -\frac{1}{Z}\frac{24\hbar^2}{m_e r_{19}^3}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.417)$$

corresponding to the 2 and $3p_x$, p_y, and p_z electrons.

As shown in the P-Orbital Electrons Based on an Energy Minimum section for $\mathbf{F}_{diamagnetic\,2}$ given by Eq. (10.93), the corresponding diamagnetic force for 2p electrons due to a relativistic effect with an electric field for $r > r_n$ (Eq. (10.35)) is dependent on the amplitude of the orbital energy. Using the orbital energy with $\ell = 1$ (Eq. (10.90)), the energy $m_e \Delta v^2$ of Eq. (10.29) is reduced by the factor of $\left(1 - \frac{\sqrt{2}}{2}\right)$ due to the contribution of the charge-density wave of the inner electrons at r_3.   In addition, it was shown in the 3P-Orbital Electrons Based on an Energy Minimum section that the two 3s electrons contribute an energy factor based on Eq. (1.82) since the filled 2p orbitals with the maintenance of symmetry according to Eq. (10.72) requires that the diamagnetic force is due to the electrons at r_{10} acing on the electrons at r_{12} which complies with the reactive force, $\mathbf{F}_{diamagnetic\,2}$, given by Eq. (10.229).   Thus, $\mathbf{F}_{diamagnetic\,2}$ for the factor from 3p

electrons with $Z > n$ is reduced by the factor of $\left(1 - \dfrac{\sqrt{2}}{2} + \dfrac{1}{2}\right)$. Similarly, the factor for 4s electrons due to the inner 2p, 3s, and 3p electrons is cumulative. Thus, $\mathbf{F}_{diamagnetic\ 2}$ for 4s electrons with $Z > n$ is

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-n}{Z-(n-1)}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2} - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{18}\hbar^2}{m_e r_n^4}10\sqrt{s(s+1)}\,\mathbf{i}_r \qquad (10.418)$$

For $n = 19$, $\mathbf{F}_{diamagnetic\ 2}$ is

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-19}{Z-18}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2} - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{18}\hbar^2}{m_e r_{19}^4}10\sqrt{s(s+1)}\,\mathbf{i}_r \qquad (10.419)$$

In the case that $Z > 19$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.407)) and diamagnetic (Eqs. (10.416), (10.417), and (10.419)) forces as follows:

$$\frac{m_e v_{19}^2}{r_{19}} = \frac{(Z-18)e^2}{4\pi\varepsilon_o r_{19}^2} - \frac{3\hbar^2}{4m_e r_{19}^2 r_{18}}\sqrt{s(s+1)} - \frac{24\hbar^2}{Zm_e r_{19}^3}\sqrt{s(s+1)}$$
$$- \left[\frac{Z-19}{Z-18}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2} - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{18}\hbar^2}{m_e r_{19}^4}10\sqrt{s(s+1)} \qquad (10.420)$$

Substitution of $v_{19} = \dfrac{\hbar}{m_e r_{19}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.420) gives:

$$\frac{\hbar^2}{m_e r_{19}^3} = \frac{(Z-18)e^2}{4\pi\varepsilon_o r_{19}^2} - \frac{3\hbar^2}{4m_e r_{19}^2 r_{18}}\sqrt{\frac{3}{4}} - \frac{24\hbar^2}{Zm_e r_{19}^3}\sqrt{\frac{3}{4}} - \left[\frac{Z-19}{Z-18}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2} - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{18}\hbar^2}{m_e r_{19}^4}10\sqrt{\frac{3}{4}}$$
$$(10.421)$$

The quadratic equation corresponding to Eq. (10.421) is

$$\left(\frac{(Z-18)e^2}{4\pi\varepsilon_o} - \frac{3\hbar^2}{4m_e r_{18}}\sqrt{\frac{3}{4}}\right)r_{19}^2 - \frac{\hbar^2}{m_e}\left(1 + \frac{24\sqrt{\frac{3}{4}}}{Z}\right)r_{19} - \left[\frac{Z-19}{Z-18}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2} - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{18}\hbar^2}{m_e}10\sqrt{\frac{3}{4}} = 0$$
$$(10.422)$$

$$r_{19}^2 - \frac{\dfrac{\hbar^2}{m_e}\left(1 + \dfrac{24\sqrt{\frac{3}{4}}}{Z}\right)}{\left(\dfrac{(Z-18)e^2}{4\pi\varepsilon_o} - \dfrac{3\hbar^2}{4m_e r_{18}}\sqrt{\frac{3}{4}}\right)}r_{19} - \frac{\left[\dfrac{Z-19}{Z-18}\right]\left(1 - \dfrac{\sqrt{2}}{2} + \dfrac{1}{2} - \dfrac{\sqrt{2}}{2} + \dfrac{1}{2}\right)\dfrac{r_{18}\hbar^2}{m_e}10\sqrt{\frac{3}{4}}}{\left(\dfrac{(Z-18)e^2}{4\pi\varepsilon_o} - \dfrac{3\hbar^2}{4m_e r_{18}}\sqrt{\frac{3}{4}}\right)} = 0$$
$$(10.423)$$

The solution of Eq. (10.423) using the quadratic formula is:

$$r_{19} = \cfrac{\cfrac{\dfrac{\hbar^2}{m_e}\left(1+\dfrac{24\sqrt{\tfrac{3}{4}}}{Z}\right)}{\left(\dfrac{(Z-18)e^2}{4\pi\varepsilon_o}-\dfrac{3\hbar^2}{4m_e r_{18}}\sqrt{\dfrac{3}{4}}\right)} \pm \sqrt{\left(\cfrac{\dfrac{\hbar^2}{m_e}\left(1+\dfrac{24\sqrt{\tfrac{3}{4}}}{Z}\right)}{\left(\dfrac{(Z-18)e^2}{4\pi\varepsilon_o}-\dfrac{3\hbar^2}{4m_e r_{18}}\sqrt{\dfrac{3}{4}}\right)}\right)^2 + 4\cfrac{\left[\dfrac{Z-19}{Z-18}\right]\left(1-\dfrac{\sqrt{2}}{2}+\dfrac{1}{2}-\dfrac{\sqrt{2}}{2}+\dfrac{1}{2}\right)\dfrac{r_{18}\hbar^2}{m_e}10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-18)e^2}{4\pi\varepsilon_o}-\dfrac{3\hbar^2}{4m_e r_{18}}\sqrt{\dfrac{3}{4}}\right)}}}{2}$$

$$(10.424)$$

$$r_{19} = \cfrac{\cfrac{a_0\left(1+\dfrac{12\sqrt{3}}{Z}\right)}{\left((Z-18)-\dfrac{3\sqrt{3}}{8r_{18}}\right)} \pm a_0 \sqrt{\left(\cfrac{1+\dfrac{12\sqrt{3}}{Z}}{\left((Z-18)-\dfrac{3\sqrt{3}}{8r_{18}}\right)}\right)^2 + \cfrac{20\sqrt{3}\left(\left[\dfrac{Z-19}{Z-18}\right]\left(1-\dfrac{\sqrt{2}}{2}+\dfrac{1}{2}-\dfrac{\sqrt{2}}{2}+\dfrac{1}{2}\right)r_{18}\right)}{\left((Z-18)-\dfrac{3\sqrt{3}}{8r_{18}}\right)}}}{2}$$

$$(10.425)$$

r_{18} *in units of* a_0

where r_{18} is given by Eq. (10.399). The positive root of Eq. (10.425) must be taken in order that $r_{19} > 0$.   The radii of several nineteen-electron atoms are given in Table 10.19.

The ionization energies for the nineteen-electron atoms with $Z > 19$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii r_{19}, given by Eq. (10.425)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-18)e^2}{8\pi\varepsilon_o r_{19}} \qquad (10.426)$$

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured nineteen-electron atoms are given in Table 10.19.

Table 10.19. Ionization energies for some nineteen-electron atoms.

19 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_{10} (a_o) [c]	r_{12} (a_o) [d]	r_{18} (a_o) [e]	r_{19} (a_o) [f]	Theoretical Ionization Energies [g] (eV)	Experimental Ionization Energies [h] (eV)	Relative Error [i]
K	19	0.05302	0.22503	0.26884	0.71450	0.85215	3.14515	4.32596	4.34066	0.0034
Ca^+	20	0.05035	0.21308	0.25149	0.65725	0.82478	2.40060	11.3354	11.87172	0.0452
Sc^{2+}	21	0.04794	0.20235	0.23625	0.60857	0.76196	1.65261	24.6988	24.75666	0.0023
Ti^{3+}	22	0.04574	0.19264	0.22276	0.56666	0.70013	1.29998	41.8647	43.2672	0.0324
V^{4+}	23	0.04374	0.18383	0.21074	0.53022	0.64511	1.08245	62.8474	65.2817	0.0373
Cr^{5+}	24	0.04191	0.17579	0.19995	0.49822	0.59718	0.93156	87.6329	90.6349	0.0331
Mn^{6+}	25	0.04022	0.16842	0.19022	0.46990	0.55552	0.81957	116.2076	119.203	0.0251
Fe^{7+}	26	0.03867	0.16165	0.18140	0.44466	0.51915	0.73267	148.5612	151.06	0.0165
Co^{8+}	27	0.03723	0.15540	0.17336	0.42201	0.48720	0.66303	184.6863	186.13	0.0078
Ni^{9+}	28	0.03589	0.14961	0.16601	0.40158	0.45894	0.60584	224.5772	224.6	0.0001
Cu^{10+}	29	0.03465	0.14424	0.15926	0.38305	0.43379	0.55797	268.2300	265.3	-0.0110
Zn^{11+}	30	0.03349	0.13925	0.15304	0.36617	0.41127	0.51726	315.6418	310.8	-0.0156

[a] Radius of the paired 1s inner electrons of nineteen-electron atoms from Eq. (10.51).

[b] Radius of the paired 2s inner electrons of nineteen-electron atoms from Eq. (10.62).

[c] Radius of the three sets of paired 2p inner electrons of nineteen-electron atoms from Eq. (10.212)).

[d] Radius of the paired 3s inner electrons of nineteen-electron atoms from Eq. (10.255)).

[e] Radius of the three sets of paired 3p inner electrons of nineteen-electron atoms from Eq. (10.399)

[f] Radius of the unpaired 4s outer electron of nineteen-electron atoms from Eq. (10.425) for $Z > 19$ and Eq. (10.414) for K.

[g] Calculated ionization energies of nineteen-electron atoms given by the electric energy (Eq. (10.426)).

[h] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].

[i] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.19 is well within the experimental capability of the spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy. In this case, the experimental capability is about three to four significant figures which is consistent with the last column. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed. Thus, the potassium atom isoelectronic series given in Table 10.19 [2-3] relies on theoretical calculations and interpolation of the K isoelectronic and Rydberg series as well as direct experimental data to extend the precision beyond the capability of X-ray spectroscopy. But, no assurances can be given that these techniques are correct, and they may not improve

the results.   The error given in the last column is very reasonable given the quality of the data.

TWENTY-ELECTRON ATOMS

Twenty-electron atoms can be solved exactly using the results of the solutions of one, two, three, four, five, six, seven, eight, nine, ten, eleven, twelve, thirteen, fourteen, fifteen, sixteen, seventeen, eighteen, and nineteen-electron atoms.

RADIUS AND IONIZATION ENERGY OF AN OUTER ELECTRON OF THE CALCIUM ATOM

For each nineteen-electron atom having a central charge of Z times that of the proton, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by Eq. (7.19) (Eq. (10.51)), two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by Eq. (10.62), three sets of paired electrons in an orbitsphere at r_{10} given by Eq. (10.212), two indistinguishable spin-paired electrons in an orbitsphere with radii r_{11} and r_{12} both given by Eq. (10.255), three sets of paired electrons in an orbitsphere with radius r_{18} given by Eq. (10.399), and an unpaired electron in an orbitsphere with radius r_{19} given by Eq. (10.425).   For $Z \geq 20$, the next electron which binds to form the corresponding twenty-electron atom is attracted by the central Coulomb field and the spin-pairing force with the unpaired 4s inner electron and is repelled by diamagnetic forces due to the 3 sets of spin-paired inner 3p electrons such that it forms and unpaired orbitsphere at radius r_{20}.

The central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner nineteen electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-19)e^2}{4\pi\varepsilon_o r_{20}^2}\mathbf{i}_r \tag{10.427}$$

for $r > r_{19}$.

The forces for the calcium atom follow from those of the magnesium atom given in the Twelve-Electron Atom section.   The outer electron which binds to form the corresponding twenty-electron atom becomes spin-paired with the unpaired inner electron such that they become indistinguishable with the same radius $r_{19} = r_{20}$ corresponding to a filled 4s shell.   The corresponding spin-pairing force $\mathbf{F}_{mag}$ is given by Eqs. (7.15) and (10.239):

$$\mathbf{F}_{mag} = \frac{1}{Z} \frac{\hbar^2}{m_e r_{20}^3} \sqrt{s(s+1)} \mathbf{i}_r \qquad (10.428)$$

The spherically symmetrical closed 3p shell of twenty-electron atoms produces a diamagnetic force, $\mathbf{F}_{diamagnetic}$, that is equivalent to that of a closed s shell given by Eq. (10.11) with the appropriate radii. The inner electrons remain at their initial radii, but cause a diamagnetic force according to Lenz's law that is

$$\mathbf{F}_{diamagnetic} = -\frac{\hbar^2}{4 m_e r_{20}^2 r_{18}} \sqrt{s(s+1)} \mathbf{i}_r \qquad (10.429)$$

In addition to the paramagnetic spin-pairing force between the nineteenth electron initially at radius r_{19}, the pairing causes the diamagnetic interaction between the outer electrons and the inner electrons given by Eq. (10.11) to vanish, except for an electrodynamic effect for $Z > 20$ described in the Two-Electron Atoms section, since upon pairing the magnetic field of the outer electrons becomes zero. Using Eqs. (10.55) and (10.240), $\mathbf{F}_{mag\,2}$ due to the three 3p orbitals is given by:

$$\mathbf{F}_{mag\,2} = \frac{3}{Z} \frac{\hbar^2}{m_e r_{20} r_{18}^2} \sqrt{s(s+1)} \mathbf{i}_r \qquad (10.430)$$

In addition to the spin-spin interactions between electron pairs, the three sets of 2p and 3p electrons are orbitally paired. The 4s electrons of the calcium atom produce a magnetic field at the position of the six sets of spin-paired 2p and 3p electrons which interact as described in the P-Orbital Electrons Based on an Energy Minimum section. In order for the electrons to remain spin and orbitally paired, the corresponding diamagnetic force, $\mathbf{F}_{diamagnetic\,3}$, on electron twenty from the six sets of spin-paired electrons that follows from the deviation given in the Eleven-Electron Atom section (Eq. (10.221)) is

$$\mathbf{F}_{diamagnetic\,3} = -\frac{1}{Z} \frac{24\hbar^2}{m_e r_{20}^3} \sqrt{s(s+1)} \mathbf{i}_r \qquad (10.431)$$

corresponding to the 2 and $3 p_x$, p_y, and p_z electrons.

The outward centrifugal force on electron 20 is balanced by the electric force and the magnetic forces (on electron 20). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.427)), diamagnetic (Eq. (10.428-10.429) and (10.431)), and paramagnetic (Eq. (10.430)) forces as follows:

$$\frac{m_e v_{20}^2}{r_{20}} = \frac{(Z-19)e^2}{4\pi\varepsilon_o r_{20}^2} - \frac{\hbar^2}{4 m_e r_{20}^2 r_{18}} \sqrt{s(s+1)} + \frac{3\hbar^2}{Z m_e r_{20}^2 r_{18}} \sqrt{s(s+1)}$$

$$- \frac{24\hbar^2}{Z m_e r_{20}^3} \sqrt{s(s+1)} + \frac{\hbar^2}{Z m_e r_{20}^3} \sqrt{s(s+1)} \qquad (10.432)$$

Substitution of $v_{20} = \dfrac{\hbar}{m_e r_{20}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.432) gives:

$$\frac{\hbar^2}{m_e r_{20}^3} = \frac{(Z-18)e^2}{4\pi\varepsilon_o r_{20}^2} - \frac{\hbar^2}{4m_e r_{20}^2 r_{18}}\sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Zm_e r_{20}^2 r_{18}}\sqrt{\frac{3}{4}}$$

$$- \frac{24\hbar^2}{Zm_e r_{20}^3}\sqrt{\frac{3}{4}} + \frac{\hbar^2}{Zm_e r_{20}^3}\sqrt{\frac{3}{4}} \tag{10.433}$$

$$r_{20} = \frac{\dfrac{\hbar^2}{m_e}\left(1 + \dfrac{23\sqrt{\dfrac{3}{4}}}{Z}\right)}{\dfrac{(Z-19)e^2}{4\pi\varepsilon_o} - \left(\dfrac{1}{4} - \dfrac{3}{Z}\right)\dfrac{\hbar^2}{m_e r_{18}}\sqrt{\dfrac{3}{4}}} \tag{10.434}$$

$$r_{20} = \frac{a_0\left(1 + \dfrac{23\sqrt{\dfrac{3}{4}}}{Z}\right)}{(Z-19) - \left(\dfrac{1}{4} - \dfrac{3}{Z}\right)\dfrac{\sqrt{\dfrac{3}{4}}}{r_{18}}}, \ r_{18} \text{ in units of } a_0 \tag{10.435}$$

Substitution of $\dfrac{r_{18}}{a_0} = 0.82478$ (Eq. (10.399) with $Z = 20$) into Eq. (10.435) gives

$$r_{20} = 2.23009 a_0 \tag{10.436}$$

The ionization energy of the calcium atom is given by the electric energy, $E(electric)$, (Eq. (10.102) with the radius, r_{20}, given by Eq. (10.435)):

$$E(ionization; \ Ca) = -Electric \ Energy = \frac{(Z-19)e^2}{8\pi\varepsilon_o r_{20}} = 6.10101 \ eV \tag{10.437}$$

where $r_{20} = 2.23009 a_0$ (Eq. (10.435)) and $Z = 20$. The experimental ionization energy of the calcium atom is 6.11316 eV [3].

THE IONIZATION ENERGIES OF TWENTY-ELECTRON ATOMS WITH A NUCLEAR CHARGE Z>20

Nineteen-electron atoms having $Z > 20$ possess an external electric field given by Eq. (10.92). Since there is a source of dissipative, $\mathbf{J} \bullet \mathbf{E}$ of Eq. (10.27), the magnetic moments of the inner electrons may change due to the outer electron such that the energy of the nineteen-electron atom is lowered. The spherically symmetrical closed 3p shell of twenty-electron atoms produces a diamagnetic force, $\mathbf{F}_{diamagnetic}$, that is equivalent to that of a closed s shell given by Eq. (10.11) with the appropriate radii except that the force is doubled (Eq. (10.96)) due to the interaction of the

2p, 3s, and 3p electrons as discussed in the 3P-Orbital Electrons Based on an Energy Minimum section with the cancellation of the contribution of the 3s orbital by the 4s orbital. The inner electrons remain at their initial radii, but cause a diamagnetic force according to Lenz's law that is

$$\mathbf{F}_{diamagnetic} = -\frac{2\hbar^2}{4m_e r_{20}^2 r_{18}}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.438)$$

In addition to the spin-spin interaction between electron pairs, the six sets of 2p and 3p electrons are orbitally paired. As in given in the Eleven-Electron Atom section, the single 4s orbital of each twenty-electron atoms having $Z > 20$ produces a magnetic field at the position of the six sets of spin-paired 2p and 3p electrons. In order for the electrons to remain spin and orbitally paired, the corresponding diamagnetic force, $\mathbf{F}_{diamagnetic\,3}$, on electron twenty from the six sets of spin-paired electrons given by Eq. (10.221) is

$$\mathbf{F}_{diamagnetic\,3} = -\frac{1}{Z}\frac{24\hbar^2}{m_e r_{20}^3}\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.439)$$

corresponding to the 2 and $3p_x$, p_y, and p_z electrons.

From Eq. (10.418), the diamagnetic force, $\mathbf{F}_{diamagnetic\,2}$, due to a relativistic effect with an electric field for $r > r_{20}$ (Eq. (10.35)) is

$$\mathbf{F}_{diamagnetic\,2} = -\left[\frac{Z-20}{Z-19}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2} - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{18}\hbar^2}{m_e r_{20}^4}10\sqrt{s(s+1)}\mathbf{i}_r \qquad (10.440)$$

In the case that $Z > 20$, the radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (10.427)) and diamagnetic (Eqs. (10.438-10.440)) forces as follows:

$$\frac{m_e v_{20}^2}{r_{20}} = \frac{(Z-19)e^2}{4\pi\varepsilon_o r_{20}^2} - \frac{2\hbar^2}{4m_e r_{20}^2 r_{18}}\sqrt{s(s+1)} - \frac{24\hbar^2}{Zm_e r_{20}^3}\sqrt{s(s+1)}$$

$$-\left[\frac{Z-20}{Z-19}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2} - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{18}\hbar^2}{m_e r_{20}^4}10\sqrt{s(s+1)} \qquad (10.441)$$

Substitution of $v_{20} = \dfrac{\hbar}{m_e r_{20}}$ (Eq. (1.56)) and $s = \dfrac{1}{2}$ into Eq. (10.441) gives:

$$\frac{\hbar^2}{m_e r_{20}^3} = \frac{(Z-19)e^2}{4\pi\varepsilon_o r_{20}^2} - \frac{2\hbar^2}{4m_e r_{20}^2 r_{18}}\sqrt{\frac{3}{4}} - \frac{24\hbar^2}{Zm_e r_{20}^3}\sqrt{\frac{3}{4}}$$

$$-\left[\frac{Z-20}{Z-19}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2} - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{18}\hbar^2}{m_e r_{20}^4}10\sqrt{\frac{3}{4}} \qquad (10.442)$$

The quadratic equation corresponding to Eq. (10.442) is

$$r_{20}^2 - \frac{\frac{\hbar^2}{m_e}\left(1 + \frac{24\sqrt{\frac{3}{4}}}{Z}\right)}{\left(\frac{(Z-19)e^2}{4\pi\varepsilon_o} - \frac{2\hbar^2}{4m_e r_{18}}\sqrt{\frac{3}{4}}\right)} r_{20} - \frac{\left[\frac{Z-20}{Z-19}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2} - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{18}\hbar^2}{m_e}10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-19)e^2}{4\pi\varepsilon_o} - \frac{2\hbar^2}{4m_e r_{18}}\sqrt{\frac{3}{4}}\right)} = 0$$

$$(10.443)$$

The solution of Eq. (10.443) using the quadratic formula is:

$$r_{20} = \frac{\frac{\frac{\hbar^2}{m_e}\left(1 + \frac{24\sqrt{\frac{3}{4}}}{Z}\right)}{\left(\frac{(Z-19)e^2}{4\pi\varepsilon_o} - \frac{2\hbar^2}{4m_e r_{18}}\sqrt{\frac{3}{4}}\right)} \pm \sqrt{\left(\frac{\frac{\hbar^2}{m_e}\left(1 + \frac{24\sqrt{\frac{3}{4}}}{Z}\right)}{\left(\frac{(Z-19)e^2}{4\pi\varepsilon_o} - \frac{2\hbar^2}{4m_e r_{18}}\sqrt{\frac{3}{4}}\right)}\right)^2 + 4\frac{\left[\frac{Z-20}{Z-19}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2} - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)\frac{r_{18}\hbar^2}{m_e}10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-19)e^2}{4\pi\varepsilon_o} - \frac{2\hbar^2}{4m_e r_{18}}\sqrt{\frac{3}{4}}\right)}}}{2}$$

$$(10.444)$$

$$r_{20} = \frac{\frac{a_0\left(1 + \frac{12\sqrt{3}}{Z}\right)}{\left((Z-19) - \frac{\sqrt{3}}{4r_{18}}\right)} \pm a_0\sqrt{\left(\frac{1 + \frac{12\sqrt{3}}{Z}}{\left((Z-19) - \frac{\sqrt{3}}{4r_{18}}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-20}{Z-19}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2} - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)r_{18}\right)}{\left((Z-19) - \frac{\sqrt{3}}{4r_{18}}\right)}}}{2}$$

$$(10.445)$$

r_{18} *in units of* a_0

where r_{18} is given by Eq. (10.399). The positive root of Eq. (10.445) must be taken in order that $r_{20} > 0$. The final radius of electron 20, r_{20}, is given by Eq. (10.445); this is also the final radius of electron 19. The radii of several twenty-electron atoms are given in Table 10.20. The general equation for the radii of atoms having an outer s-shell is given in the

General Equation for the Radii of Atoms Having an Outer S-Shell section.

The ionization energies for the twenty-electron atoms with $Z > 20$ are given by the electric energy, $E(electric)$, (Eq. (10.102) with the radii r_{20}, given by Eq. (10.445)):

$$E(Ionization) = -Electric\ Energy = \frac{(Z-19)e^2}{8\pi\varepsilon_o r_{20}}$$ (10.446)

Since the relativistic corrections were small, the nonrelativistic ionization energies for experimentally measured twenty-electron atoms are given in Table 10.20.

Table 10.20.   Ionization energies for some twenty-electron atoms.

20 e Atom	Z	r_1 (a_o) [a]	r_3 (a_o) [b]	r_{10} (a_o) [c]	r_{12} (a_o) [d]	r_{18} (a_o) [e]	r_{20} (a_o) [f]	Theoretical Ionization Energies [g] (eV)	Experimental Ionization Energies [h] (eV)	Relative Error [i]
Ca	20	0.05035	0.21308	0.25149	0.65725	0.82478	2.23009	6.10101	6.11316	0.0020
Sc⁺	21	0.04794	0.20235	0.23625	0.60857	0.76196	2.04869	13.2824	12.79967	-0.0377
Ti²⁺	22	0.04574	0.19264	0.22276	0.56666	0.70013	1.48579	27.4719	27.4917	0.0007
V³⁺	23	0.04374	0.18383	0.21074	0.53022	0.64511	1.19100	45.6956	46.709	0.0217
Cr⁴⁺	24	0.04191	0.17579	0.19995	0.49822	0.59718	1.00220	67.8794	69.46	0.0228
Mn⁵⁺	25	0.04022	0.16842	0.19022	0.46990	0.55552	0.86867	93.9766	95.6	0.0170
Fe⁶⁺	26	0.03867	0.16165	0.18140	0.44466	0.51915	0.76834	123.9571	124.98	0.0082
Co⁷⁺	27	0.03723	0.15540	0.17336	0.42201	0.48720	0.68977	157.8012	157.8	0.0000
Ni⁸⁺	28	0.03589	0.14961	0.16601	0.40158	0.45894	0.62637	195.4954	193	-0.0129
Cu⁹⁺	29	0.03465	0.14424	0.15926	0.38305	0.43379	0.57401	237.0301	232	-0.0217
Zn¹⁰⁺	30	0.03349	0.13925	0.15304	0.36617	0.41127	0.52997	282.3982	274	-0.0307

[a] Radius of the paired 1s inner electrons of twenty-electron atoms from Eq. (10.51).
[b] Radius of the paired 2s inner electrons of twenty-electron atoms from Eq. (10.62).
[c] Radius of the three sets of paired 2p inner electrons of twenty-electron atoms from Eq. (10.212)).
[d] Radius of the paired 3s inner electrons of twenty-electron atoms from Eq. (10.255)).
[e] Radius of the three sets of paired 3p inner electrons of twenty-electron atoms from Eq. (10.399)
[f] Radius of the paired 4s outer electrons of twenty-electron atoms from Eq. (10.445) for $Z > 20$ and Eq. (10.436) for Ca.
[g] Calculated ionization energies of twenty-electron atoms given by the electric energy (Eq. (10.446)).
[h] From theoretical calculations, interpolation of isoelectronic and spectral series, and experimental data [2-3].
[i] (Experimental-theoretical)/experimental.

The agreement between the experimental and calculated values of Table 10.20 is well within the experimental capability of the

spectroscopic determinations including the values at large Z which relies on X-ray spectroscopy.   In this case, the experimental capability is about three to four significant figures which is consistent with the last column. Ionization energies are difficult to determine since the cut-off of the Rydberg series of lines at the ionization energy is often not observed. Thus, the calcium atom isoelectronic series given in Table 10.20 [2-3] relies on theoretical calculations and interpolation of the Ca isoelectronic and Rydberg series as well as direct experimental data to extend the precision beyond the capability of X-ray spectroscopy.   But, no assurances can be given that these techniques are correct, and they may not improve the results.   The error given in the last column is very reasonable given the quality of the data.

GENERAL EQUATION FOR THE RADII OF ATOMS HAVING AN OUTER S-SHELL

The derivation of the radii and energies of the 1s, 2s, 3s, and 4s electrons is given in the One-Electron Atom, the Two-Electron Atom, the Three-Electron Atoms, the Four-Electron Atoms, the Eleven-Electron Atoms, the Twelve-Electron Atoms, the Nineteen-Electron Atoms, and the Twenty-Electron Atoms sections.   Similarly, to Eqs. (10.216) and (10.447), the general equation for the radii of s electrons is given by

$$r_n = \frac{\dfrac{a_0\left(1+(C-D)\dfrac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\dfrac{A}{8}-\dfrac{B}{2Z}\right)\dfrac{\sqrt{3}}{r_m}\right)}\pm a_0\sqrt{\dfrac{\left(\dfrac{\left(1+(C-D)\dfrac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\dfrac{A}{8}-\dfrac{B}{2Z}\right)\dfrac{\sqrt{3}}{r_m}\right)}\right)^2}{} + \dfrac{20\sqrt{3}\left(\left[\dfrac{Z-n}{Z-(n-1)}\right]Er_m\right)}{\left((Z-(n-1))-\left(\dfrac{A}{8}-\dfrac{B}{2Z}\right)\dfrac{\sqrt{3}}{r_m}\right)}}}{2} \quad (10.447)$$

r_m *in units of* a_0

where Z is the nuclear charge, n is the number of electrons, r_m is the radius of the proceeding filled shell, the parameter A given in Table 10.21 corresponds to the diamagnetic force, $F_{diamagnetic}$, (Eq. (10.11)), the parameter B given in Table 10.21 corresponds to the paramagnetic force, $F_{mag\,2}$ (Eq. (10.55)), the parameter C given in Table 10.21 corresponds to the diamagnetic force, $F_{diamagnetic\,3}$, (Eq. (10.221)), the parameter D given in Table 10.21 corresponds to the paramagnetic force, F_{mag}, (Eq. (7.15)), and the parameter E given in Table 10.21 corresponds to the diamagnetic

force, $\mathbf{F}_{diamagnetic\ 2}$, (Eqs. (10.35), (10.229), and (10.418)).   The positive root of Eq. (10.447) must be taken in order that $r_n > 0$.   The radii of several n-electron atoms having an outer s shell are given in Tables 1.2, 1.4, 1.7, 10.1, 10.2, 10.10, 10.11, 10.19, and 10.20.

Table 10.21. Summary of the parameters of atoms filling the 1s, 2s, 3s, and 4s orbitals.

Atom Type	Electron Configuration	Ground State Term [a]	Orbital Arrangement of s Electrons (s state)	Diamag. Force Factor A [b]	Paramag. Force Factor B [c]	Diamag. Force Factor C [d]	Paramag. Force Factor D [e]	Diamag. Force Factor E [f]
Neutral 1 e Atom H	$1s^1$	$^2S_{1/2}$	↑ — 1s	0	0	0	0	0
Neutral 2 e Atom He	$1s^2$	$^1S_0$	↑ ↓ — 1s	0	0	0	1	0
Neutral 3 e Atom Li	$2s^1$	$^2S_{1/2}$	↑ — 2s	1	0	0	0	0
Neutral 4 e Atom Be	$2s^2$	$^1S_0$	↑ ↓ — 2s	1	0	0	1	0
Neutral 11 e Atom Na	$1s^2 2s^2 2p^6 3s^1$	$^2S_{1/2}$	↑ — 3s	1	0	8	0	0
Neutral 12 e Atom Mg	$1s^2 2s^2 2p^6 3s^2$	$^1S_0$	↑ ↓ — 3s	1	3	12	1	0
Neutral 19 e Atom K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$^2S_{1/2}$	↑ — 4s	2	0	12	0	0
Neutral 20 e Atom Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$^1S_0$	↑ ↓ — 4s	1	3	24	1	0
1 e Ion	$1s^1$	$^2S_{1/2}$	↑ — 1s	0	0	0	0	0
2 e Ion	$1s^2$	$^1S_0$	↑ ↓ — 1s	0	0	0	1	0
3 e Ion	$2s^1$	$^2S_{1/2}$	↑ — 2s	1	0	0	0	1
4 e Ion	$2s^2$	$^1S_0$	↑ ↓ — 2s	1	0	0	1	1
11 e Ion	$1s^2 2s^2 2p^6 3s^1$	$^2S_{1/2}$	↑ — 3s	1	4	8	0	$1 + \dfrac{\sqrt{2}}{2}$

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12 e Ion	$1s^2 2s^2 2p^6 3s^2$	$^1S_0$	↑ ↓ 3s	1	6	0	0	$1+\dfrac{\sqrt{2}}{2}$
19 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$^2S_{1/2}$	↑ 4s	3	0	24	0	$2-\sqrt{2}$
20 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$^1S_0$	↑ ↓ 4s	2	0	24	0	$2-\sqrt{2}$

a The theoretical ground state terms match those given by NIST [8].

b Eq. (10.11).

c Eq. (10.55).

d Eq. (10.221).

e Eq. (7.15).

f Eqs. (10.35), (10.229), and (10.418).

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THE ELECTRON CONFIGURATION OF ATOMS

The electrons of multielectron atoms all exist as orbitspheres of discrete radii which are given by r_n of the radial Dirac delta function, $\delta(r - r_n)$.   These electron orbitspheres may be paired or unpaired depending on the force balance which applies to each electron. Ultimately, the electron configuration must be a minimum of energy. Minimum energy configurations are given by solutions to Laplace's Equation.   The general form of the solution is

$$\Phi(r, \theta, \phi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} B_{\ell,m} r^{-(\ell+1)} Y_\ell^m(\theta, \phi) \tag{11.1}$$

As demonstrated previously, this general solution gives the functions of the resonant photons.   This general solution is also the minimum energy configuration for any atom.   The configuration is given by the product of this general solution and the sum of the Dirac delta functions comprising the discrete radii of the electron orbitspheres.   In general, as shown in the One-Electron Atom section, the Two-Electron Atom section, and the Three, Four, Five, Six, Seven, Eight, Nine, Ten. Eleven, Twelve, Thirteen, Fourteen, Fifteen, Sixteen, Seventeen, Eighteen, Nineteen, and Twenty-Electron Atoms section, the electron configuration of an atom approximately parallels that of the excited modes of the helium atom: 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d. (See Excited States of Helium section.)

In general, electrons of an atom with the same principal and ℓ quantum numbers align parallel until each of the m_ℓ levels are occupied, and then pairing occurs until each of the m_ℓ levels contain paired electrons.   Exceptions occur due to the relative importance of spin and orbital interactions and paramagnetic, diamagnetic, and electric forces for a given atom or ion.